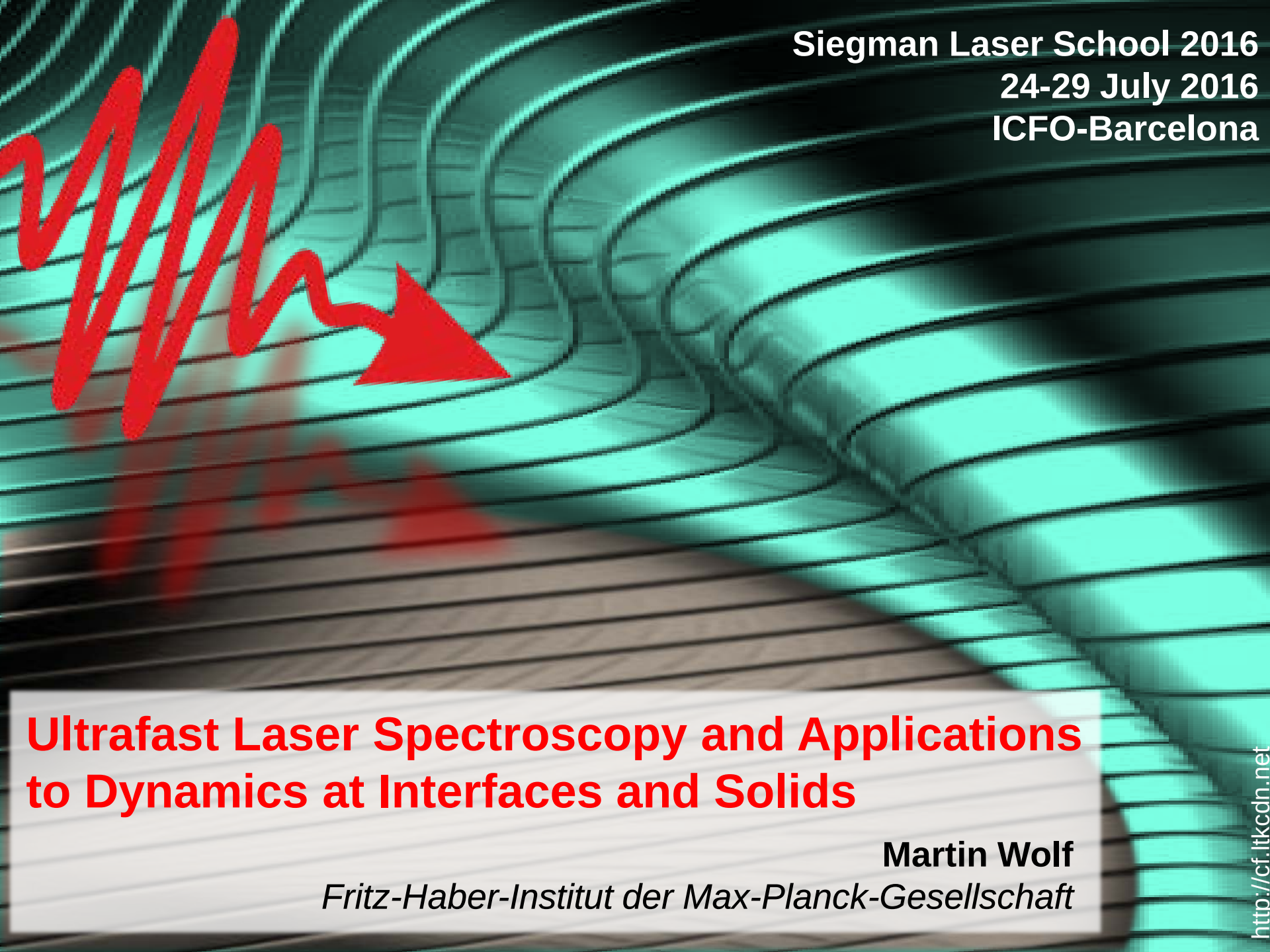


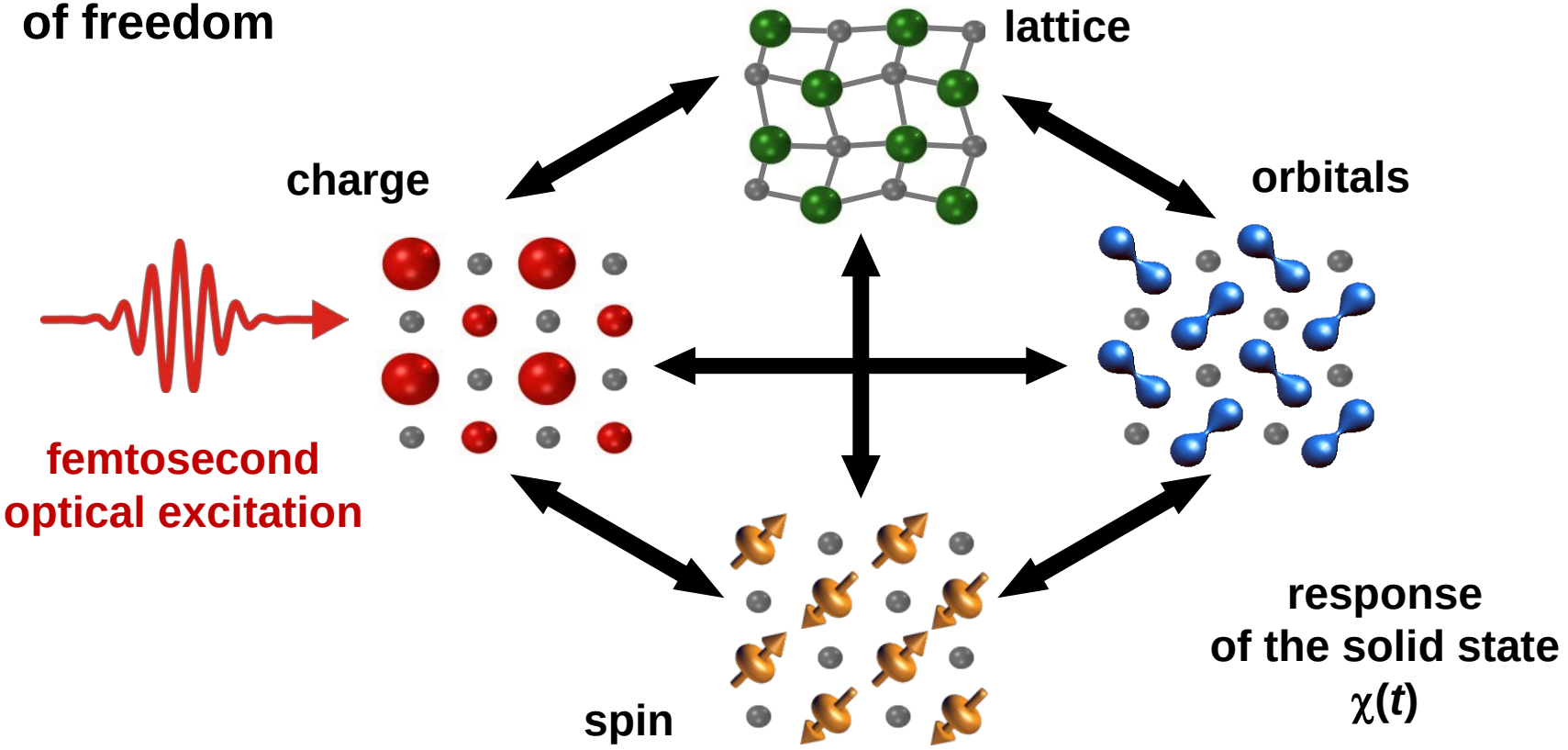
Siegman Laser School 2016
24-29 July 2016
ICFO-Barcelona

Ultrafast Laser Spectroscopy and Applications to Dynamics at Interfaces and Solids

Martin Wolf
Fritz-Haber-Institut der Max-Planck-Gesellschaft

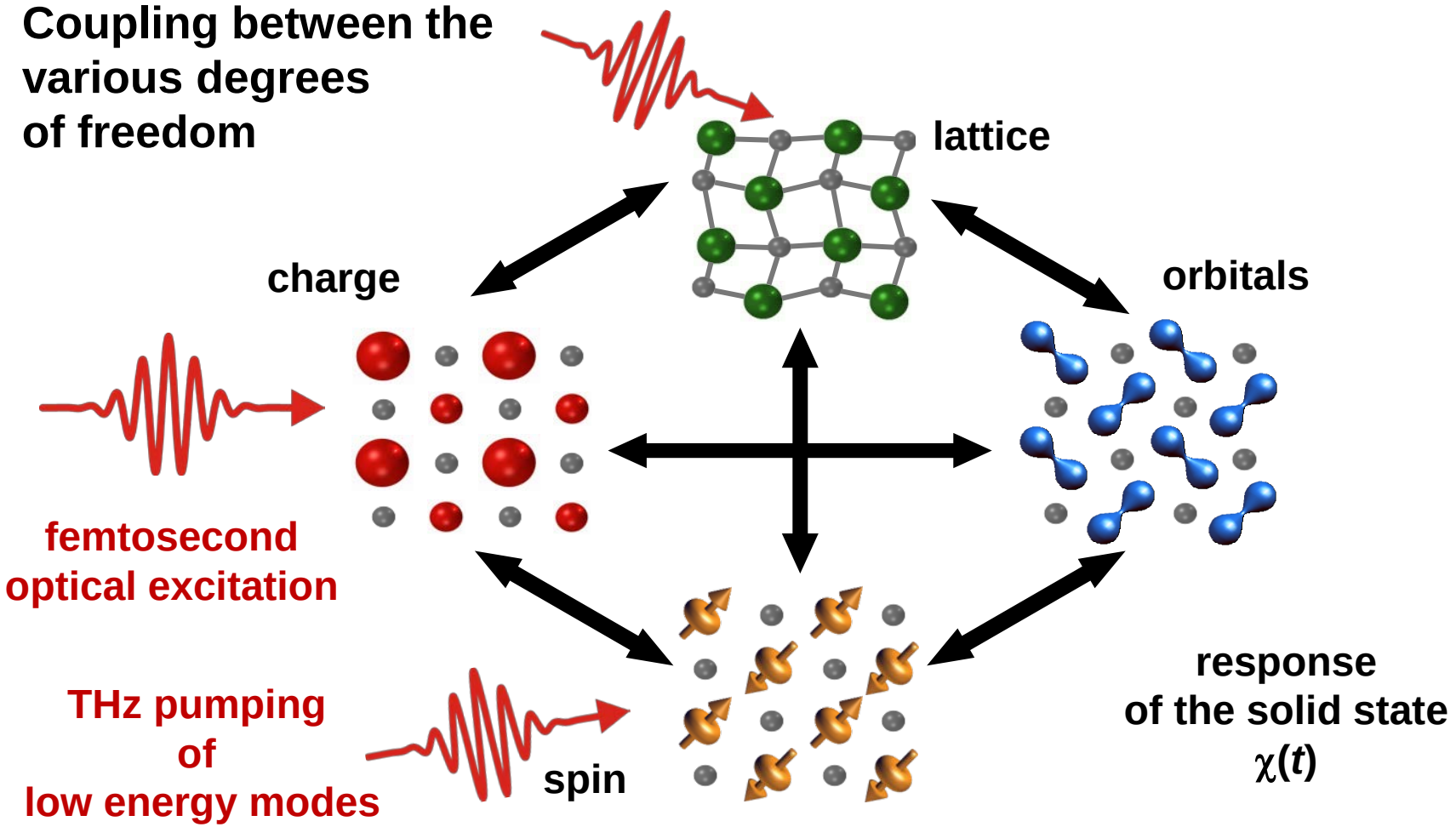
Motivation: Elementary interactions in solids

Coupling between the various degrees of freedom



Goal: Mechanistic understanding of the coupling and energy flow between the subsystems governing ultrafast phenomena

Motivation: Elementary interactions in solids



Goal: Mechanistic understanding of the coupling and energy flow between the subsystems governing ultrafast phenomena

Can phonon pumping induce phase transitions ?

Phase transitions in solids induced by optical phonon pumping

Control of the electronic phase of a manganite by mode-selective vibrational excitation

Matteo Rini[1], Ra'anan Tobey[2], Nicky Dean[2], Jiro Itatani[1,3], Yasuhide Tomioka[4], Yoshinori Tokura[4,5], Robert W. Schoenlein[1] & Andrea Cavalleri[2,6]

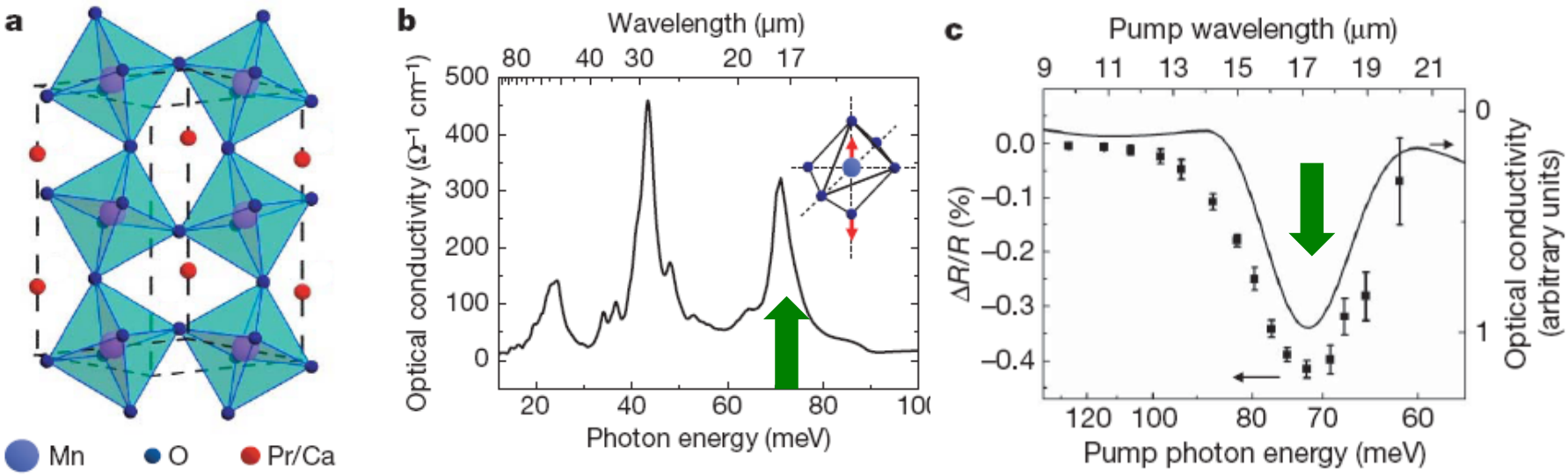


Figure 1 | $Pr_{0.7}Ca_{0.3}MnO_3$ crystal structure and vibrational spectrum.

Insulator-to-metal transition driven by resonant phonon excitation

M. Rini *et. al*, Nature **449**, 73 (2007)

Driving material response by intense THz fields

- Excitation of magnons in NiO by a THz magnetic field pulse
- Two photon excitation and phase control of a Raman active mode in diamond

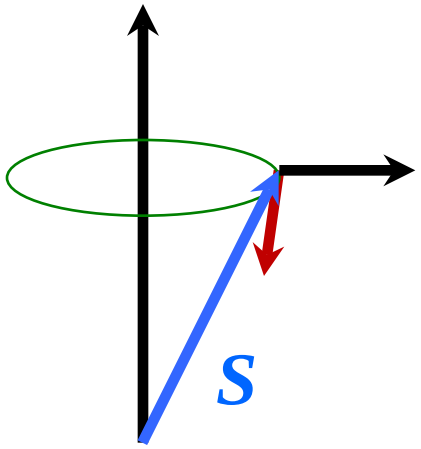
Ultrafast spin control

How to control spins as fast as possible?

most natural stimulus: magnetic field $B(t)$

$\Rightarrow$ Zeeman torque

$$T = \gamma S \times (B_{\text{int}} + B)$$



most efficient coupling at resonance:

Larmor frequency $\omega_L = \gamma |B_{\text{int}}|$

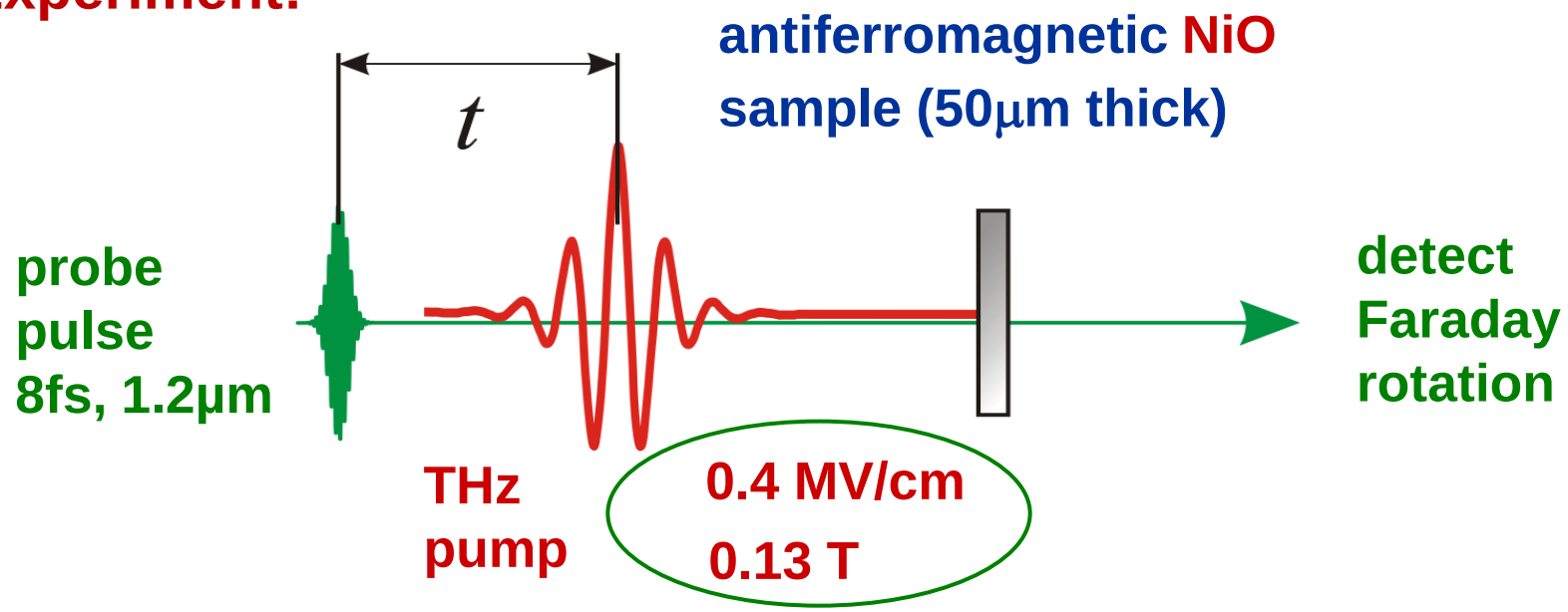
ferromagnets: < 10 GHz, **antiferromagnets: ~ 1 THz**

Hiebert, Freeman, PRL (1997)

$\Rightarrow$ apply strong THz magnetic field pulse to antiferromagnet

Experiment: THz pump – infrared probe

Experiment:

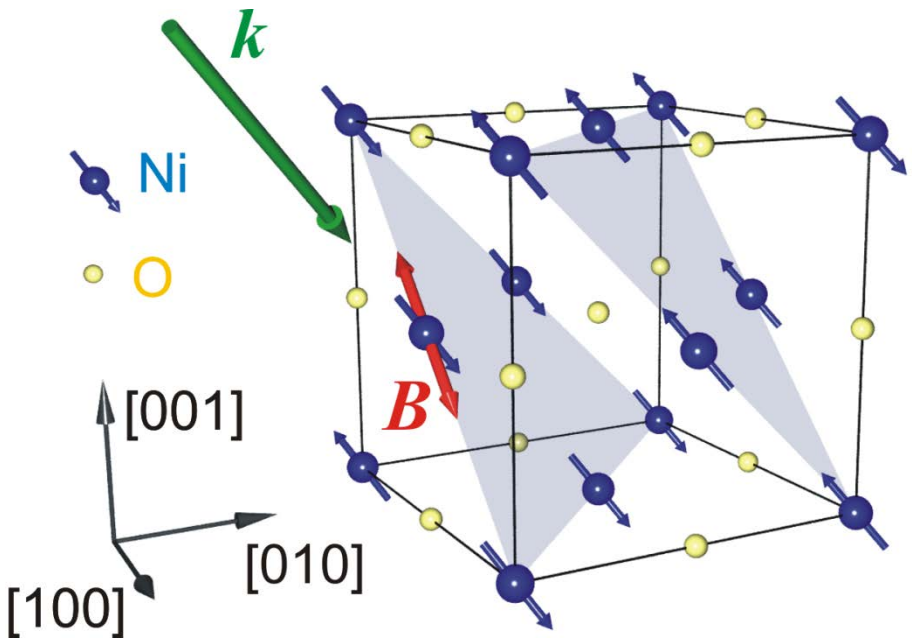


Idea:

THz magnetic field pulse induces transient magnetization which is detected via Faraday rotation of optical probe pulse

realized for ferromagnets below 10 GHz see e.g. Hiebert, Freeman, PRL (1997

NiO: A ‚textbook' antiferromagnet

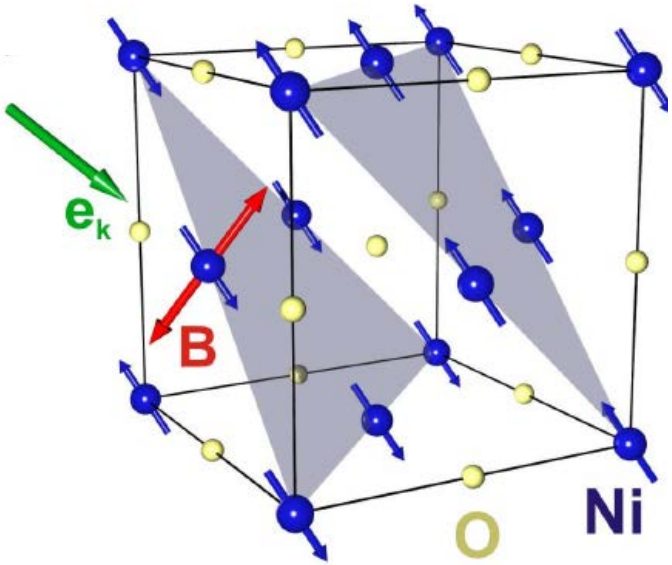


NiO lattice structure

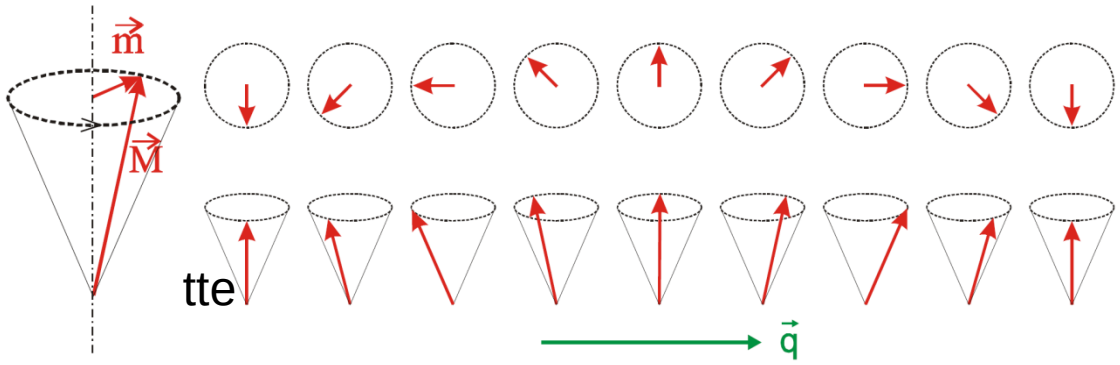
- adjacent (111) planes have opposite Ni^{2+} spins
- antiferromagnet with Neel temperature of 523K
- collective spin resonance (q = 0 magnon) at 1THz

Sievers *et al.*, PRL (1963)

NiO: A ‚textbook' antiferromagnet

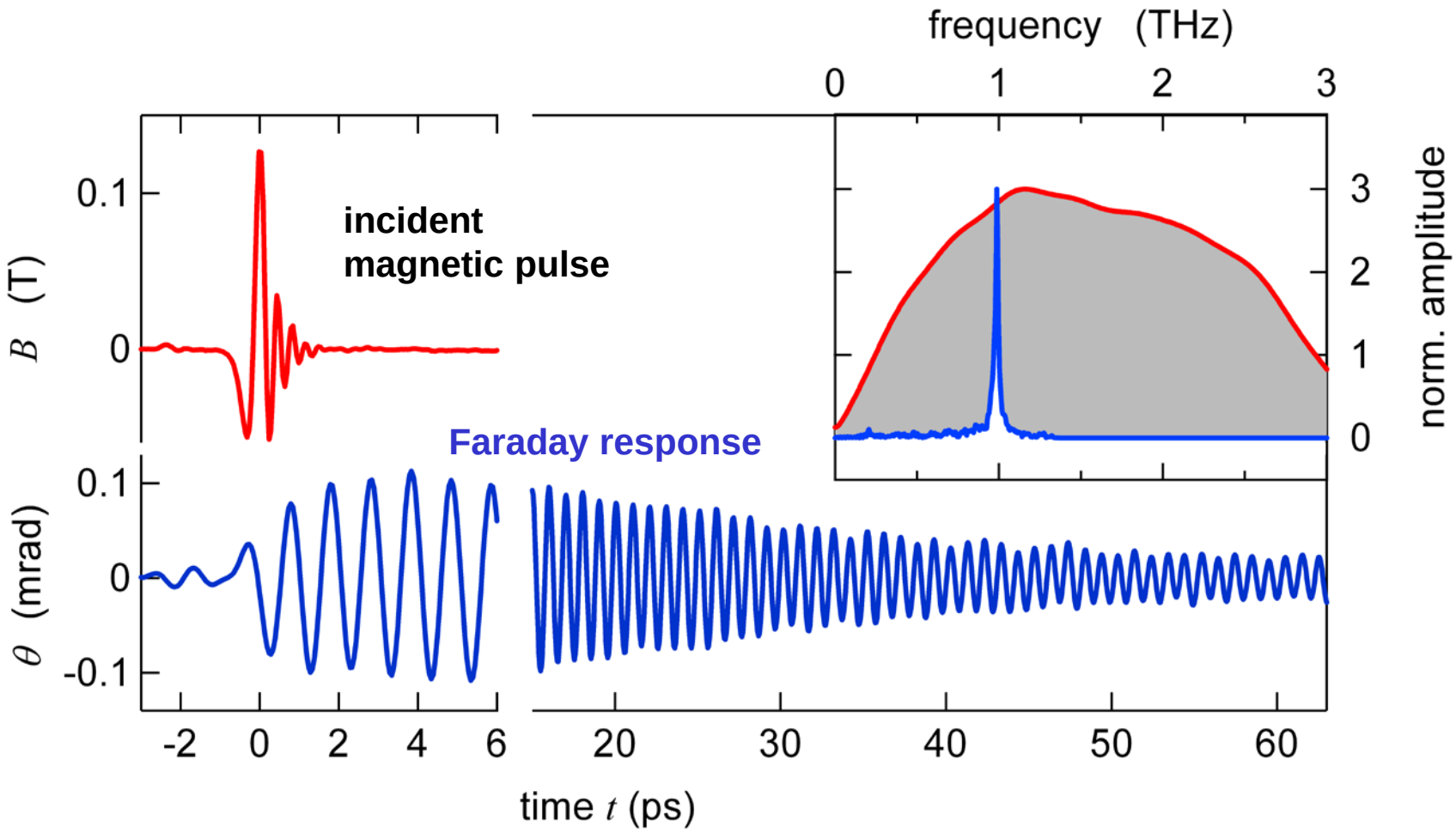


spin waves and magnons



- adjacent (111) planes have opposite Ni^{2+} spins
- antiferromagnet with Neel temperature of 523K
- collective spin resonance (q = 0 magnon) at 1THz

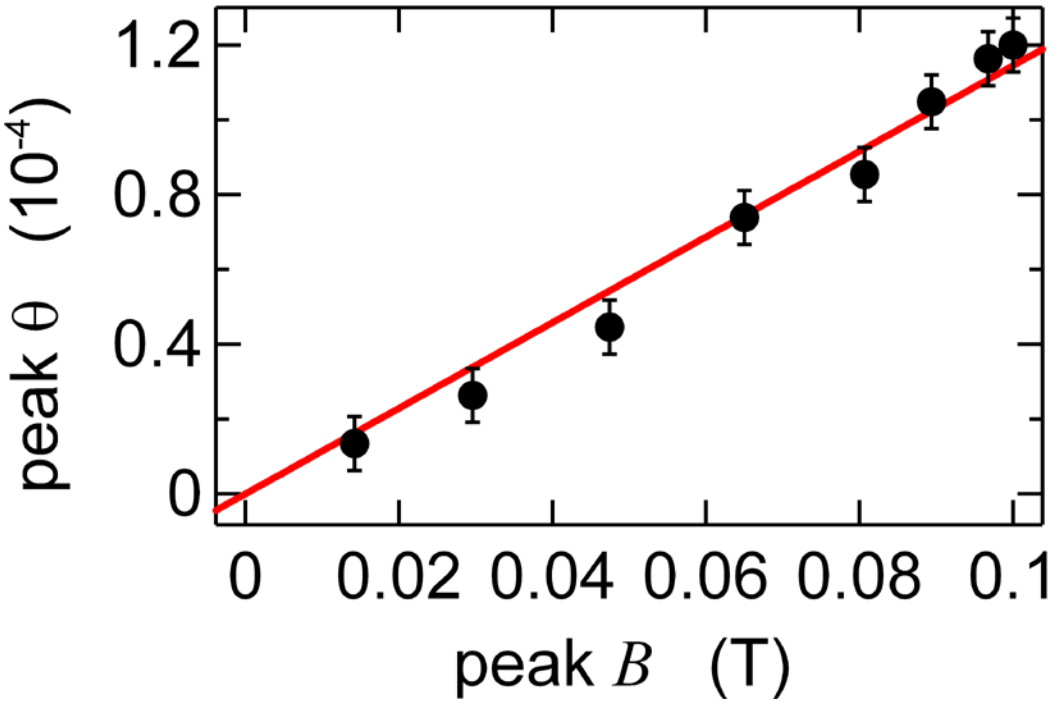
Sievers *et al.*, PRL (1963)



oscillation at 1THz, decay time 40ps

⇒ signature of $q = 0$ magnon at 1THz

Spinwave driven by magnetic field



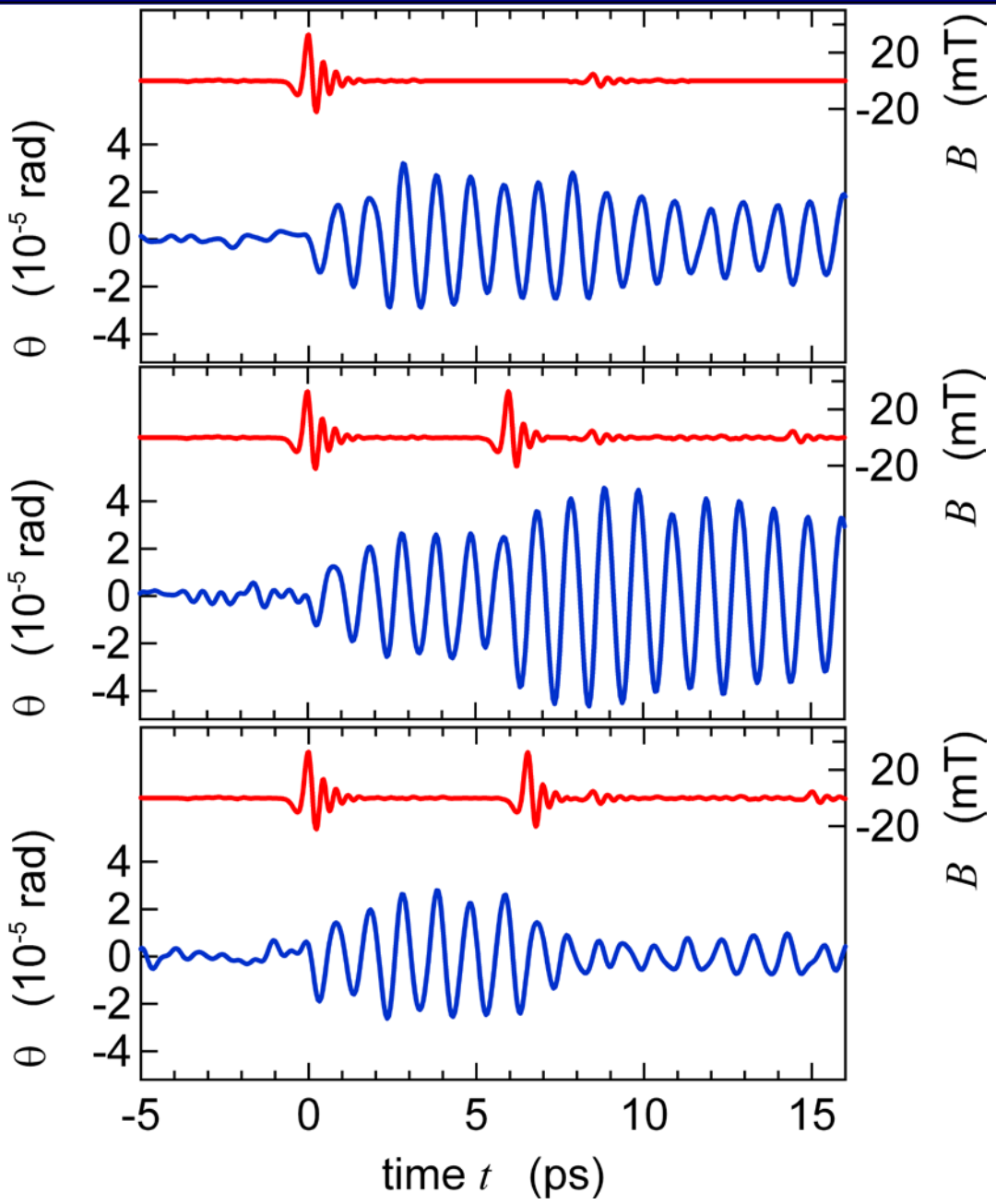
Observation: induced magnetization ∝ driving field

⇒ driving force is the magnetic (not electric) field !

⇒ free carrier and lattice excitation negligible

(NiO is insulating & all optical phonons > 12 THz)

Coherent spin control with THz pulses



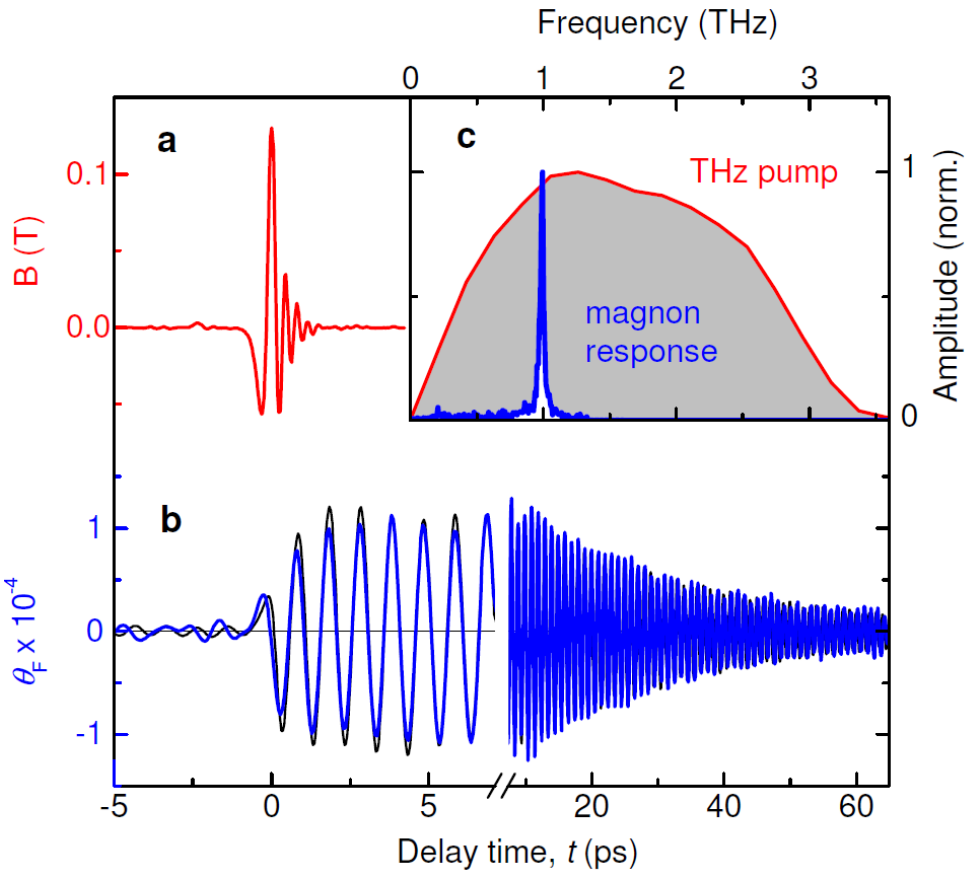
first THz pulse
excites magnon

second pulse
after 6ps
amplifies magnon

second pulse
after 6.5ps
switches
magnon off

Discussion

Zeeman-torque driven coherent THz magnon in the time domain



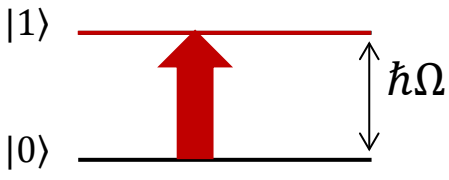
Benefits of coherent control with THz magnatic fields:

- does not require spin-orbit coupling
- no parasitic two-photon absorption
- fields up-scalable without sample destruction

T. Kampfrath *et. al*, Nature Photonics 5, 31 (2011)

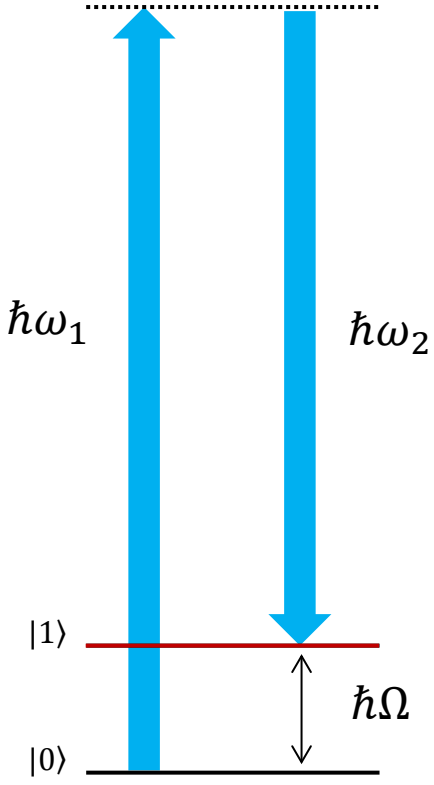
Excitation of IR or Raman active phonon modes

IR active



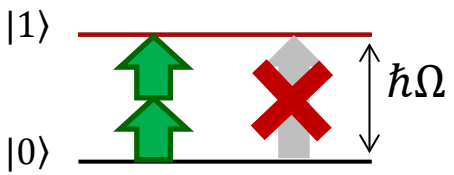
resonant
one photon
IR excitation

Raman active



stimulated
difference frequency
Raman excitation
(SRS)

Coherent lattice excitation of Raman mode via **non-resonant** two-photon absorption ?



2 photon
sum frequency
Raman excitation

Equation of motion

$$\ddot{Q} = \underbrace{-\frac{\partial V}{\partial Q}}_{\text{e.g. harmonic oscillator}} + \underbrace{E\frac{\partial P(Q,0)}{\partial Q}}_{\text{direct}} + \underbrace{\mathrm{E}^2\frac{\partial \chi(Q)}{\partial Q}}_{\text{Raman-type}}$$

Raman-tensor

= 0 (Raman mode, not IR active)

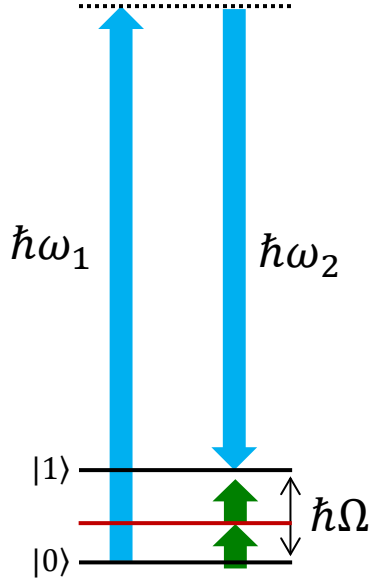
$$E(t) = \Re\mathrm{e}\left[A_1\mathrm{e}^{-i\omega_1 t} + A_2\mathrm{e}^{-i\omega_2 t}\right]$$

$$(E(t))^2 \sim \begin{cases} +\mathrm{e}^{-i(\omega_1-\omega_2)t} \\ +\mathrm{e}^{-i(\omega_1+\omega_2)t} \\ +c.c. \\ +\cdots \end{cases}$$

non resonant **difference** frequency

non resonant **sum** frequency

Raman excitation

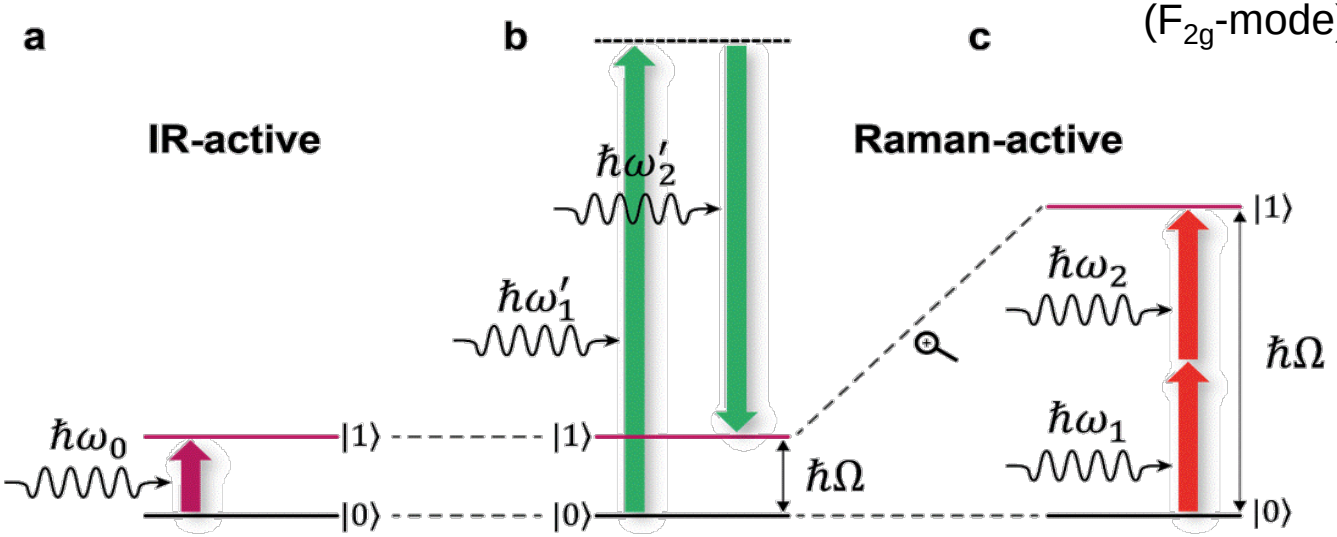


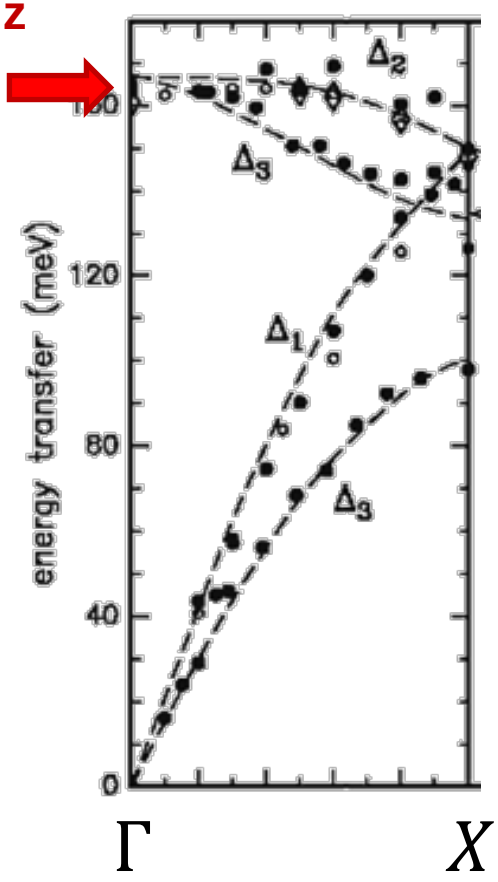
THz-pumping of F_{2g}-mode in Diamond

Non-resonant THz pumping of diamond

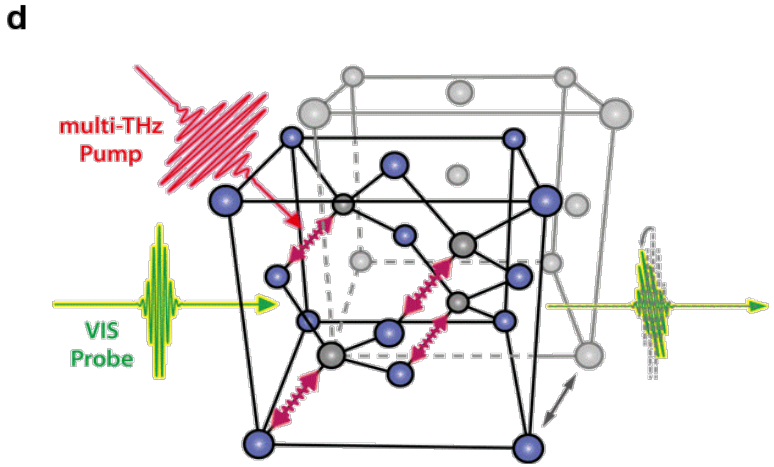
Ω = 40 THz

(F_{2g}-mode)

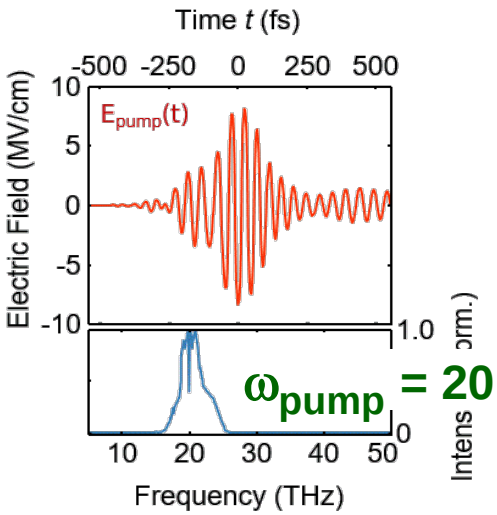




Phonon band structure of diamond

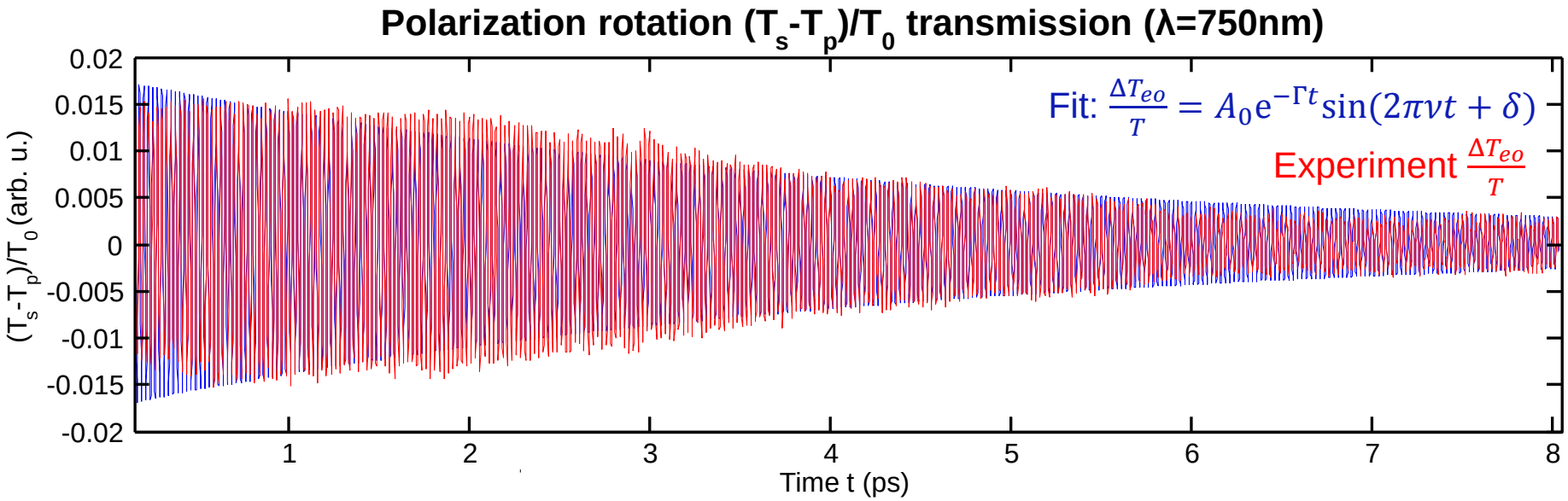


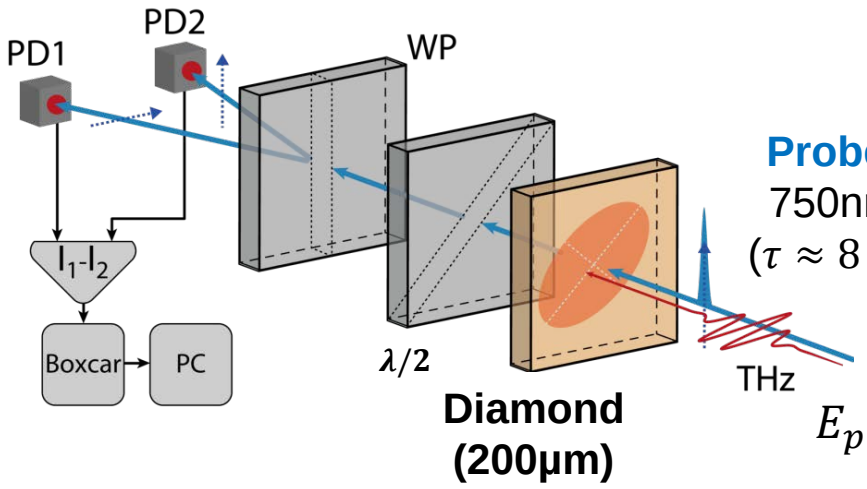
C-C stretch vibration @ 40 THz



ω_{pump} = 20 THz

THz-pumping of F_{2g}-mode in Diamond

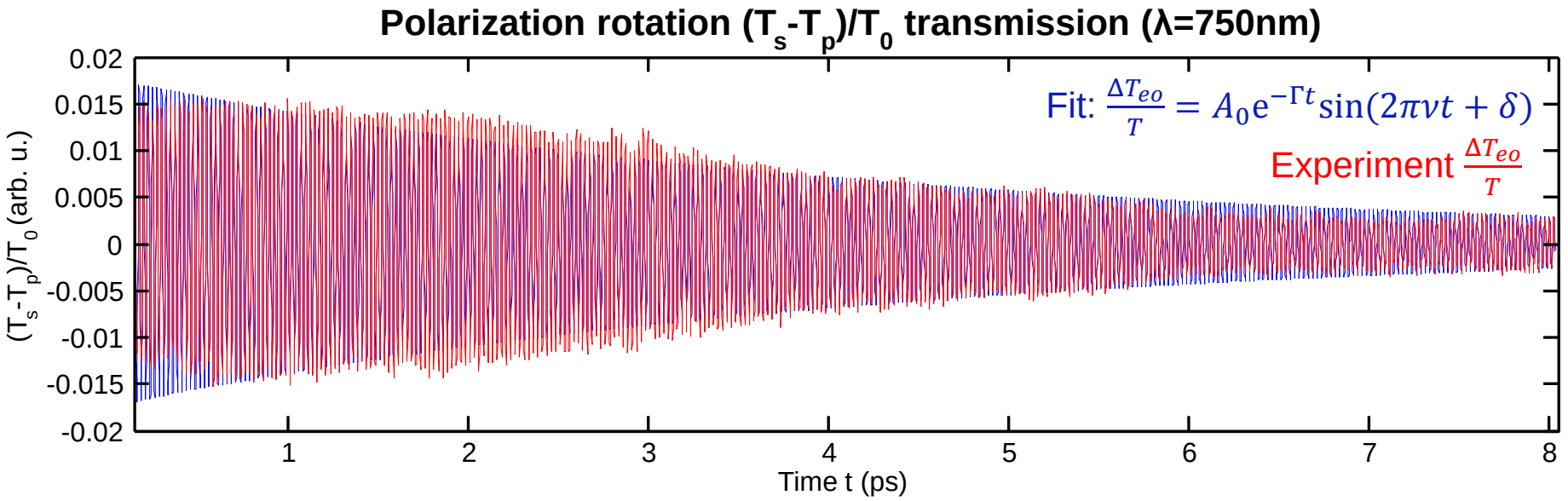


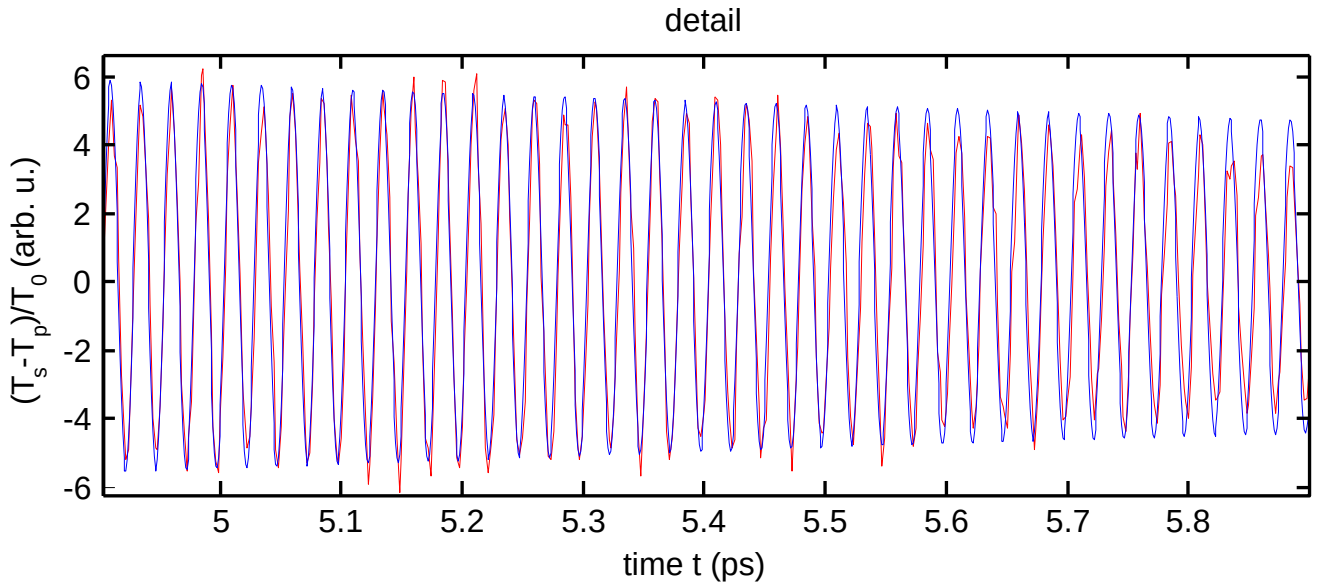


Probe:
750nm
($\tau \approx 8$ fs)

Pump:
$E_p \approx 3 - 10$ μJ
@ **20 THz**
($\tau \approx 150$ fs)

THz-pumping of F_{2g}-mode in Diamond





Fit results:

$\Gamma = 0.229\ \mathrm{ps}^{-1}$

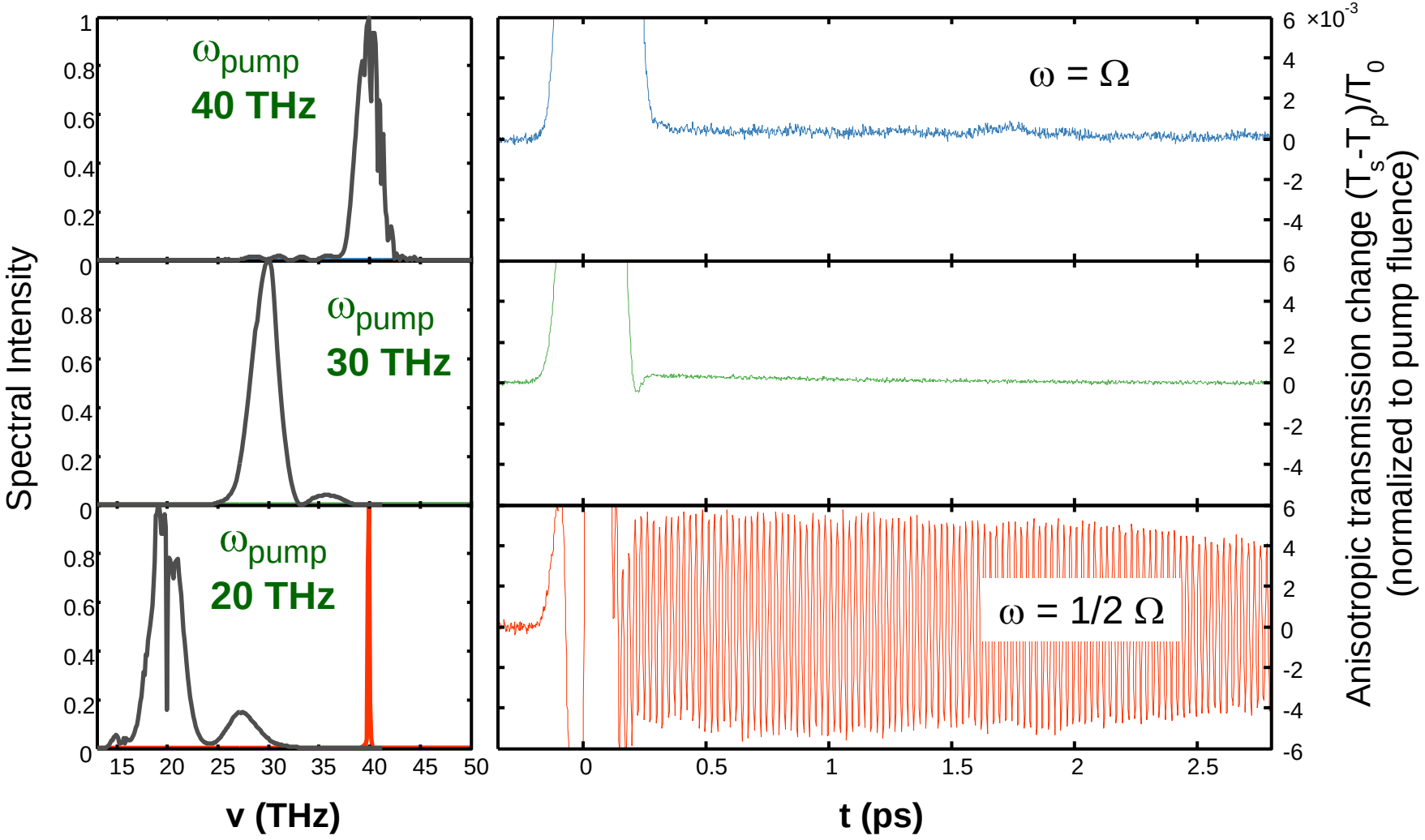
$\boldsymbol{\nu = 39.95\ \mathrm{THz}}$

consitent with
Ishioka et al, APL 2006 :

$\Gamma = 0.145\ \mathrm{ps}^{-1}$

$\nu = 39.84\ \mathrm{THz}$

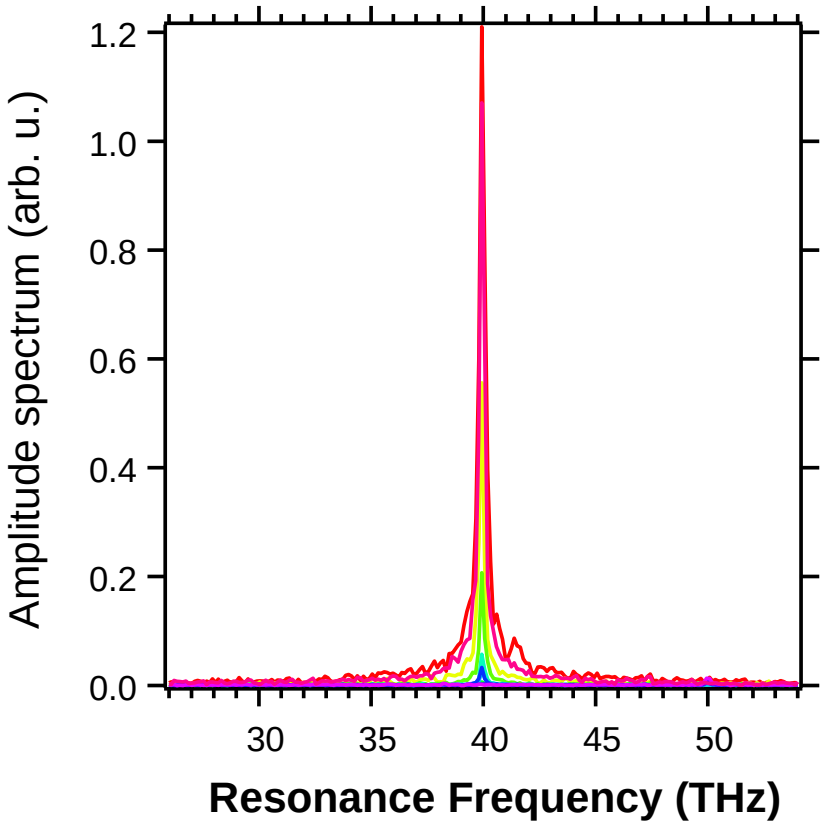
Dependence on excitation frequency

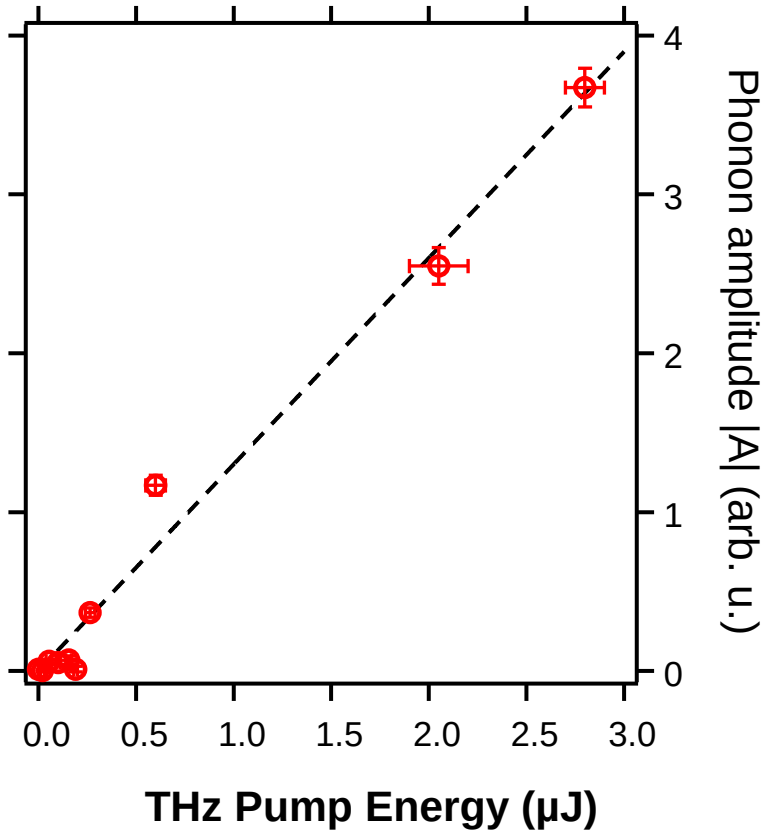


Coherent excitation of the F_{2g} phonon at **half-resonance** frequency $\omega = 1/2\Omega$

Is this a sum frequency Raman process ?

check fluence dependence





✓ Central frequency independent

✓ Damping constant independent

✓ **Phonon amplitude** $\sim I \sim E^2$

✓ Raman tensor symmetry

Demonstration of sum frequency Raman excitation

Benefits of sum frequency Raman excitation

Sum frequency Raman excitation allows to actively control the phase of coherent phonons by setting a pump pulse with dedicated carrier envelope phase (CEP) !

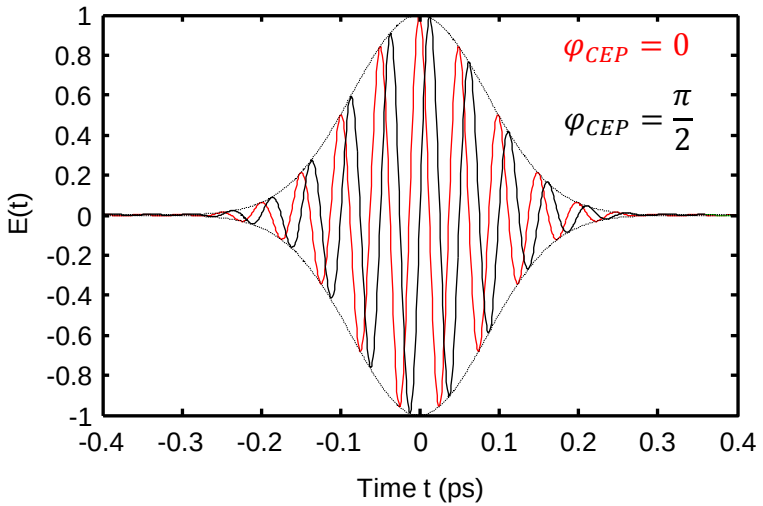
$$\rightarrow E(t) = A_1 \mathrm{e}^{-\mathrm{i}\omega_1 t + \varphi_{\mathrm{CEP}}} + A_2 \mathrm{e}^{-\mathrm{i}\omega_2 t + \varphi_{\mathrm{CEP}}} + \mathrm{c.c.}$$

difference frequency Raman excitation

$$[E(t)]^2 \sim \mathrm{e}^{-i(\omega_1 - \omega_2)t} + \mathrm{c.c.}$$

sum frequency Raman excitation

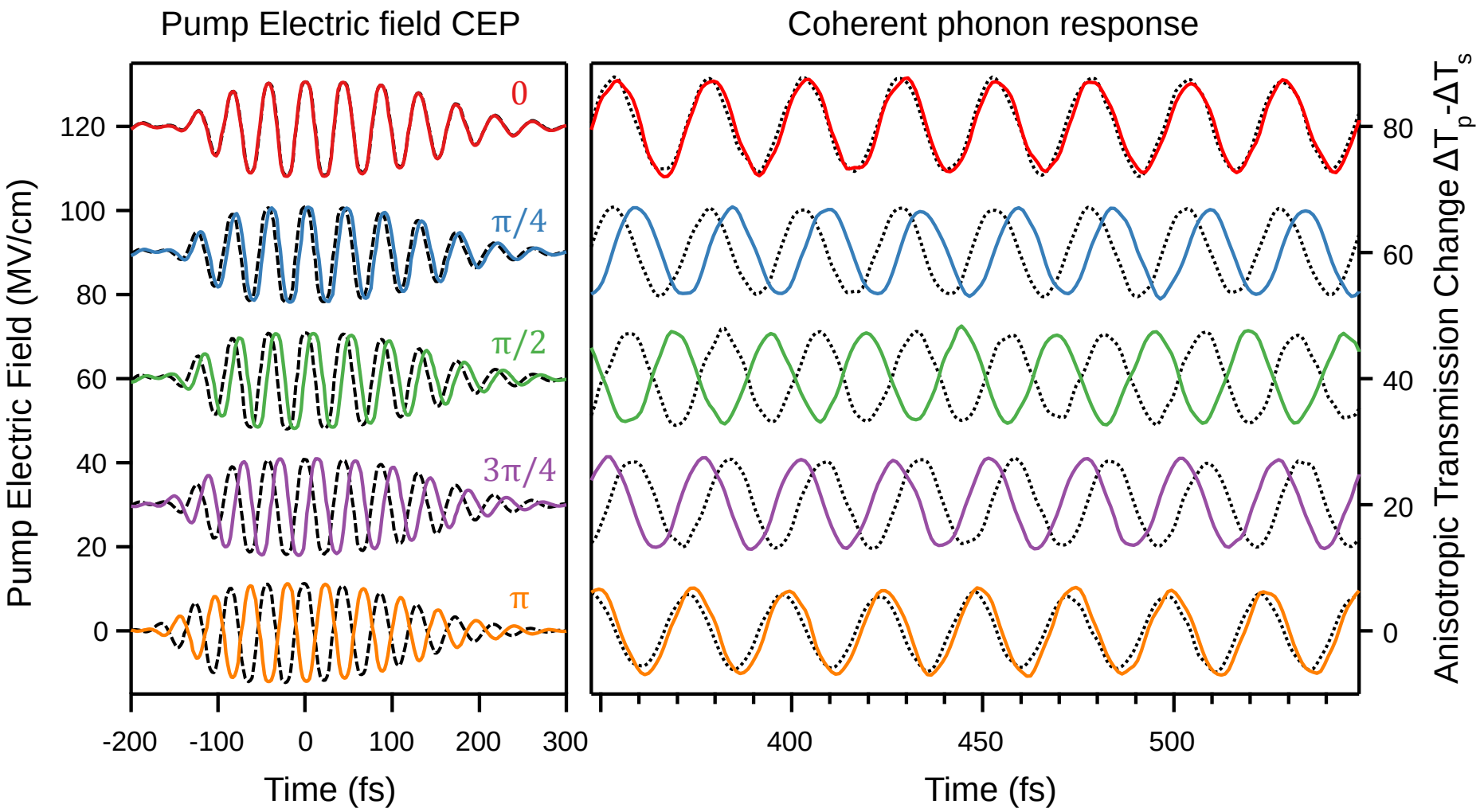
$$[E(t)]^2 \sim \mathrm{e}^{-i(\omega_1 + \omega_2)t + 2\varphi_{CEP}} + \mathrm{c.c.}$$



THz generation scheme:
difference-frequency mixing in GaSe of 2 phase-correlated infrared pulses

→ CEP phase controlled by delay

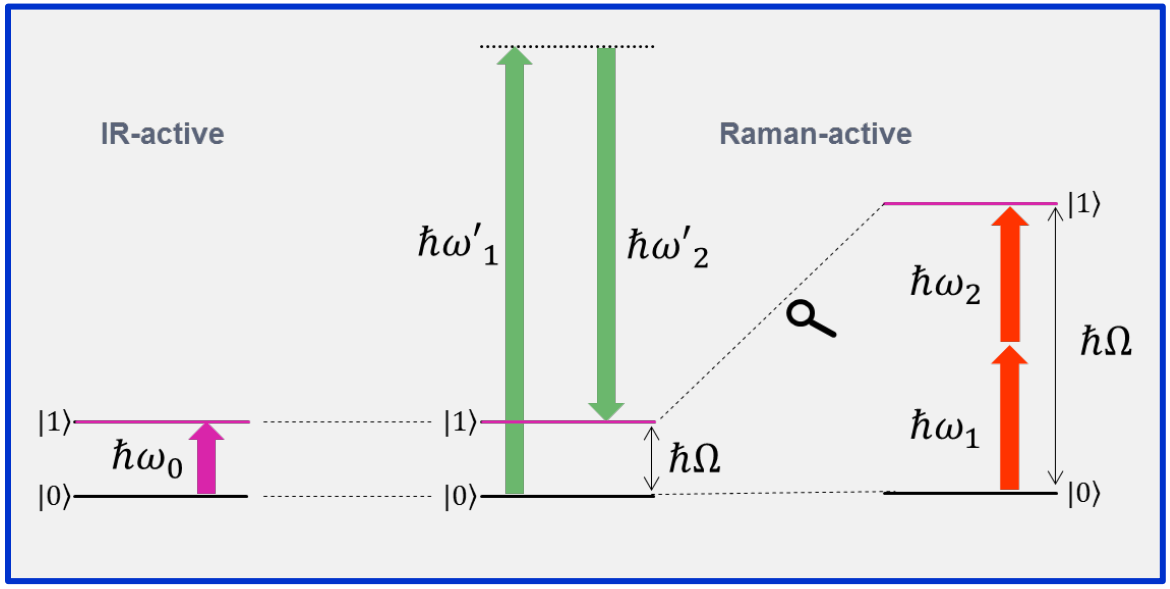
Phase Control via the THz-CEP



→ as expected: $\varphi_{\mathrm{phonon}} = 2 \cdot \phi_{\mathrm{CEP}}$

Light field CEP is imprinted on the coherent phonon phase!

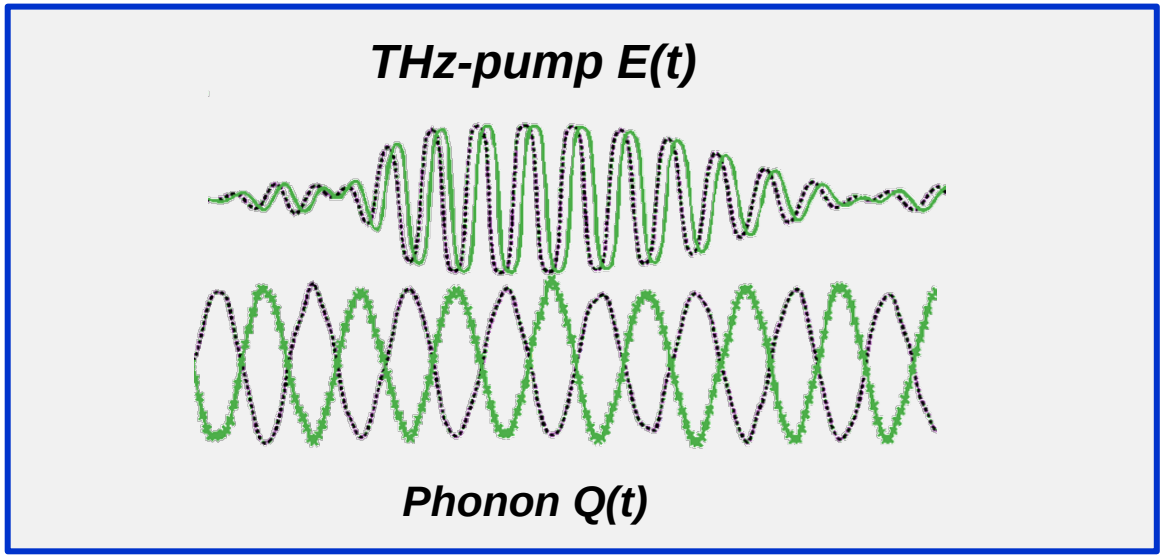
Discussion



New mechanism for coherent phonon excitation:

sum frequency Raman excitation

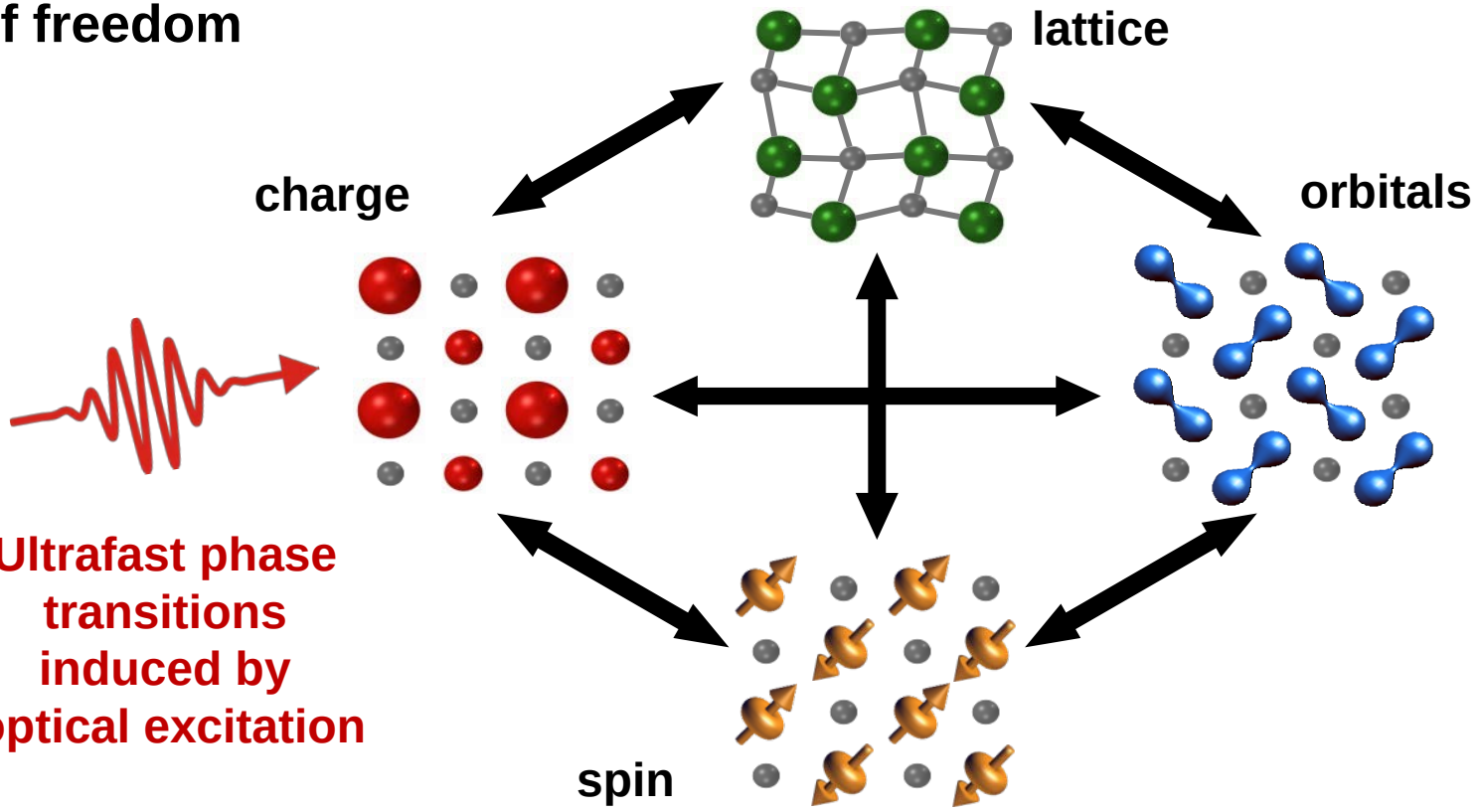
prevents parasitic electronic excitations



Coherent control of the **phonon phase** via control of THz-pump CEP

Motivation: Elementary interactions in solids

Coupling between the various degrees of freedom



Ultrafast phase transitions induced by optical excitation

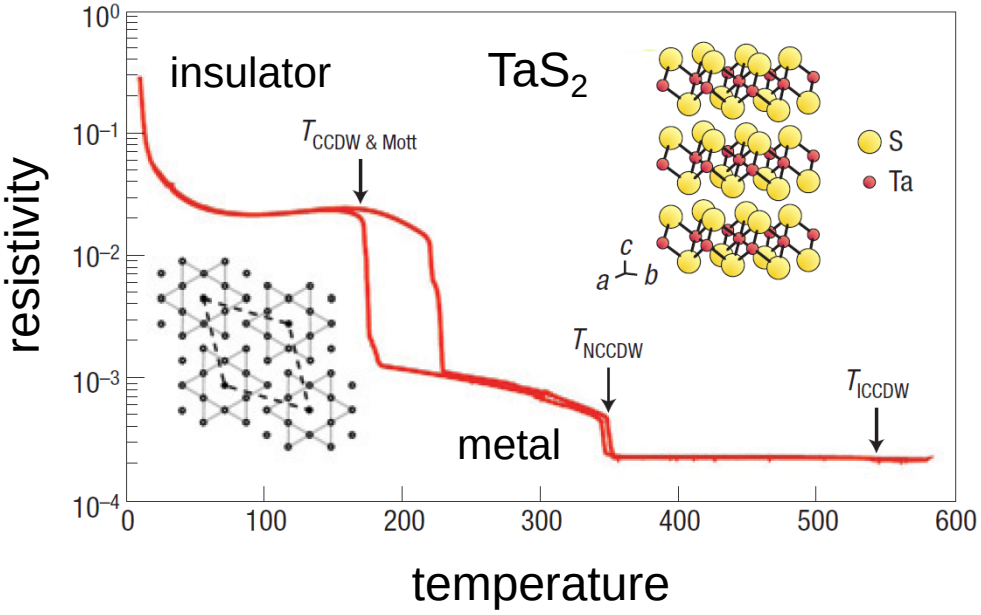
Goal: Mechanistic understanding of the coupling and energy flow between the subsystems governing ultrafast phenomena

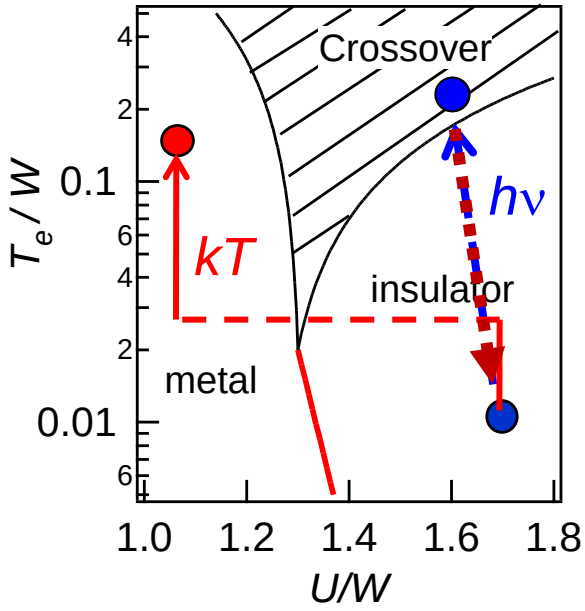
Photoinduced insulator-to-metal transition in tri-tellurides (RTe_3)

Coherent amplitude mode excitation probed by time-resolved photoemission (ARPES)

Phase transitions and ultrafast dynamics

- Phase transitions in solids (near equilibrium)
- Ultrafast photoexcitation (non-quilibrium)





optical excitation

- What can be learned from bringing the system out of equilibrium?
  - → Timescale to induce a transition to a non-equilibium state
  - → Spectroscopy of such excited states and ‚new' phases
  - → Timescale for the return to equilibrium

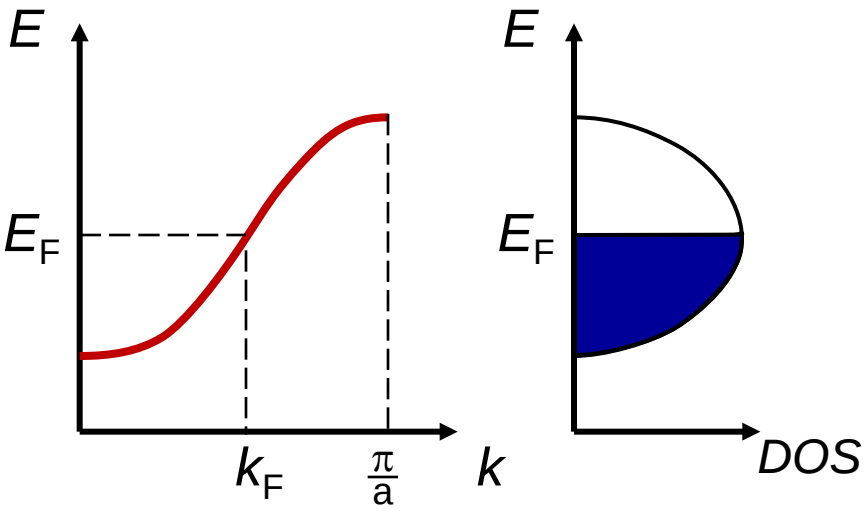
Sipos *et.al.* Nature Mater. 7, 960 (2008)

Electronic band structure of solids

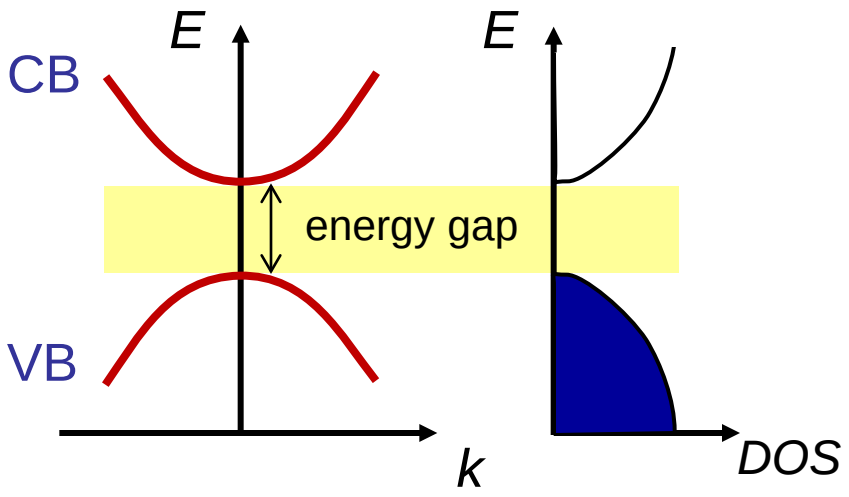
What is the origin of metallic, semiconducting and insulating behaviour?

- Use single-particle band theory (*i.e.* neglect e-e correlations)

simple metal



insulator, semiconductor

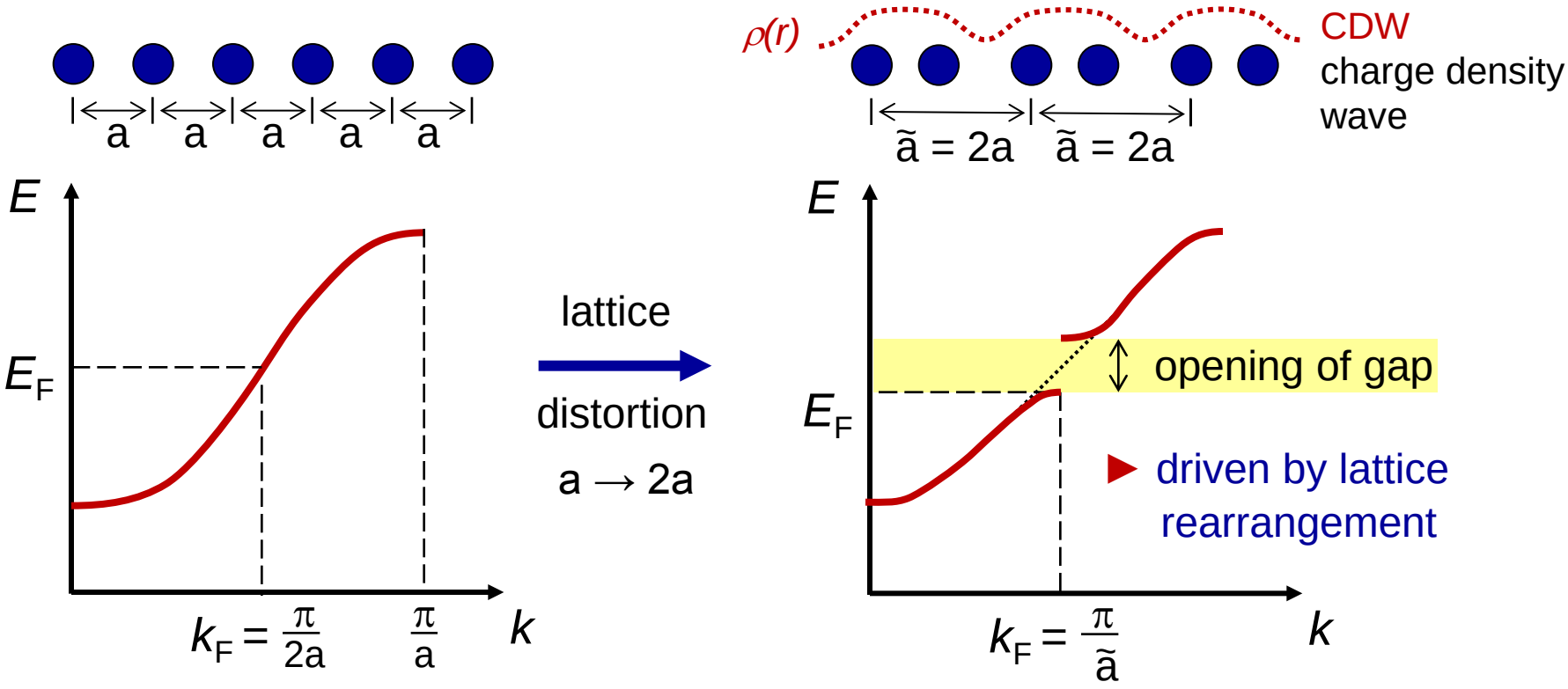


- half filled band ⇔ metal
- filled valence band ⇔ insulator or semiconductor

Charge density wave formation

Are materials with a half filled valence band always metals?

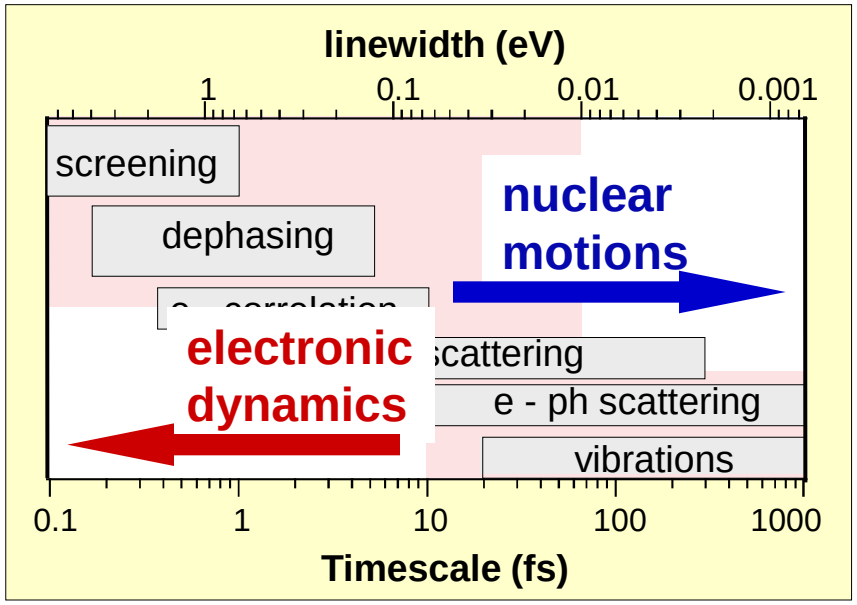
- One-dimensional metallic system with a half filled band can be unstable against lattice distortion → **Peierls instability**



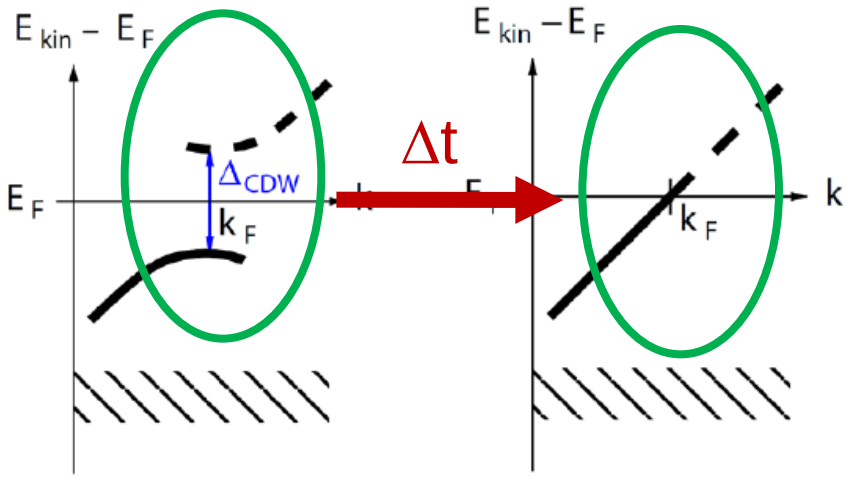
- Note: wave vector $2k_F = \frac{\pi}{a}$ fulfills Bragg reflection condition

Ultrafast photoinduced phase transitions

- What can be learned by bringing the system out of equilibrium?



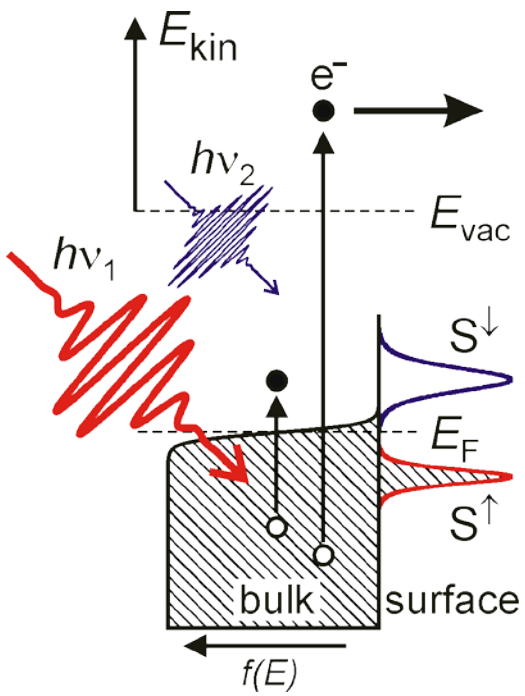
Example: Metal-Insulator transition



- Exploit separation of timescales between different processes:
  - → Timescale to induce the transition to a different phase
  - → Probing the dynamics of the order parameter
    (How fast is the gap closing ? Is there coherent dynamics)

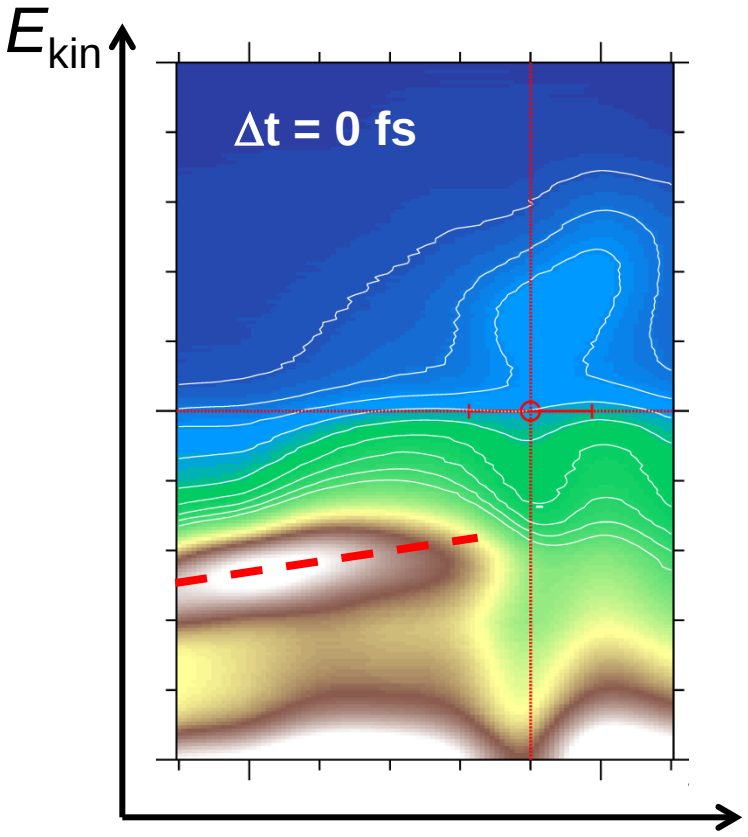
Transient electronic structure probed by trARPES

- Adding time-resolution to angle-resolved photoemission (ARPES) provides direct access to the transient electronic structure of photoexcited solids

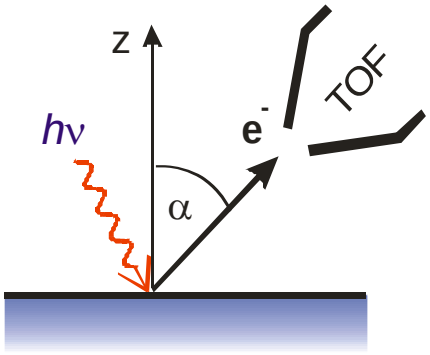


$h\nu_{pump}$ = 1.5 eV

$h\nu_{pump}$ = 6.0 eV



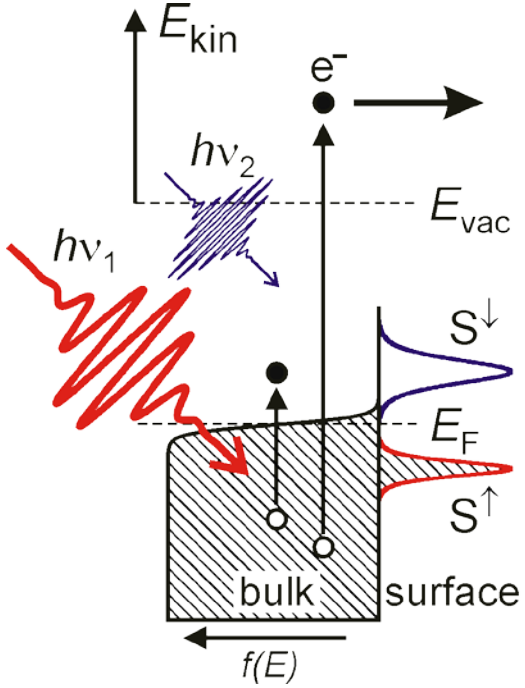
$$k_{||} = \sqrt{2m_e E_{kin}}/\hbar \cdot \sin\alpha$$



Transient electronic structure probed by trARPES

- Recording movies of photinduced changes of electronic band structure

$E(k_x,k_y,\Delta t)$

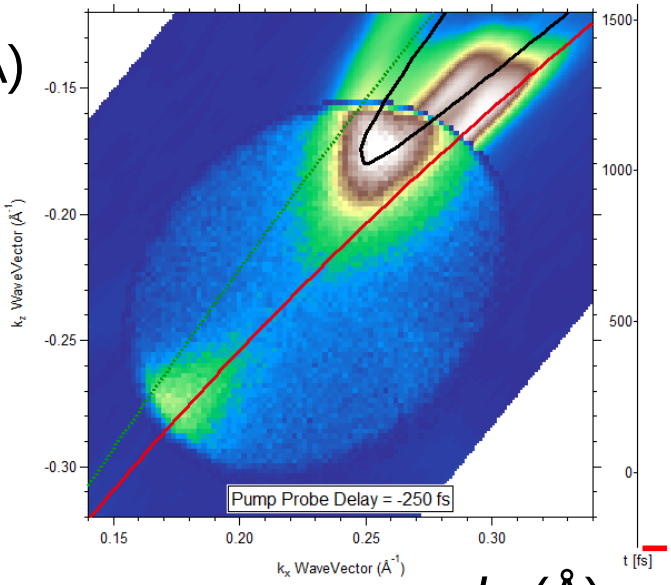


$h\nu_{pump}$ = 1.5 eV

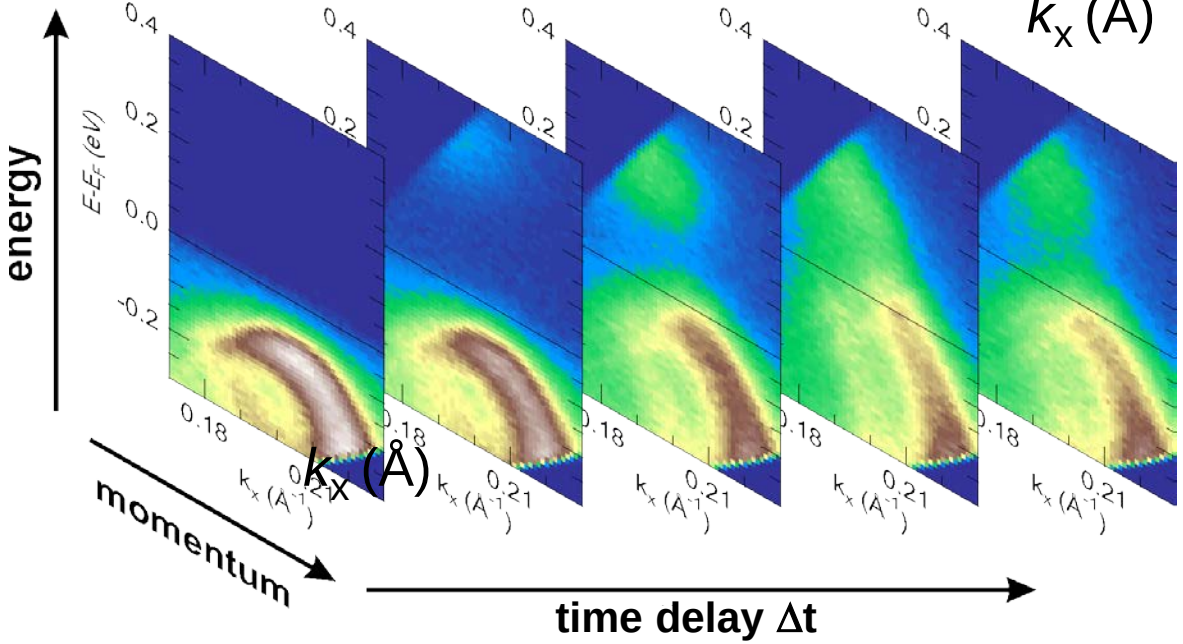
$h\nu_{pump}$ = 6.0 eV

k_Y (Å)

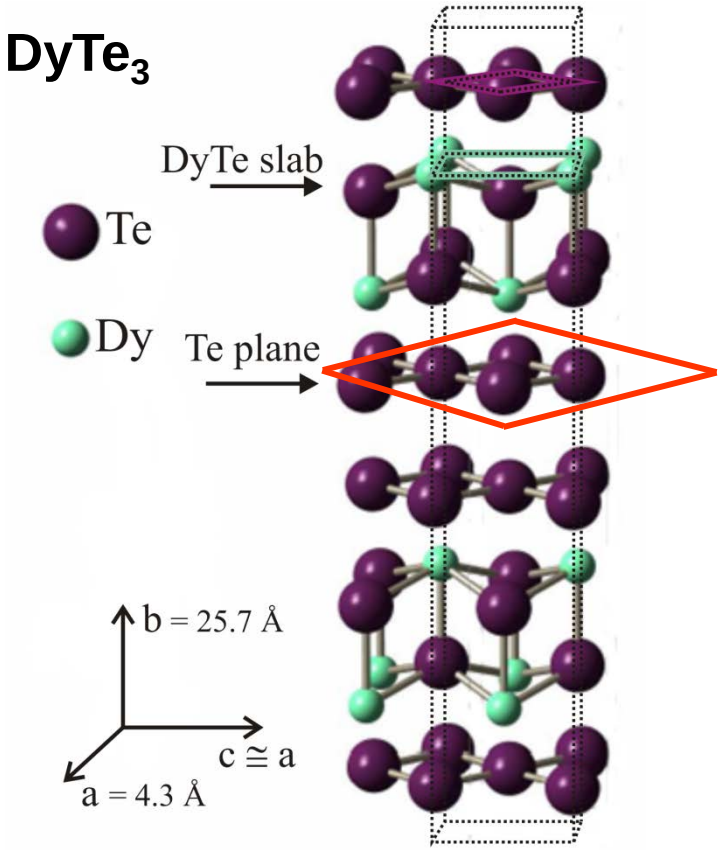
$E = E_F$



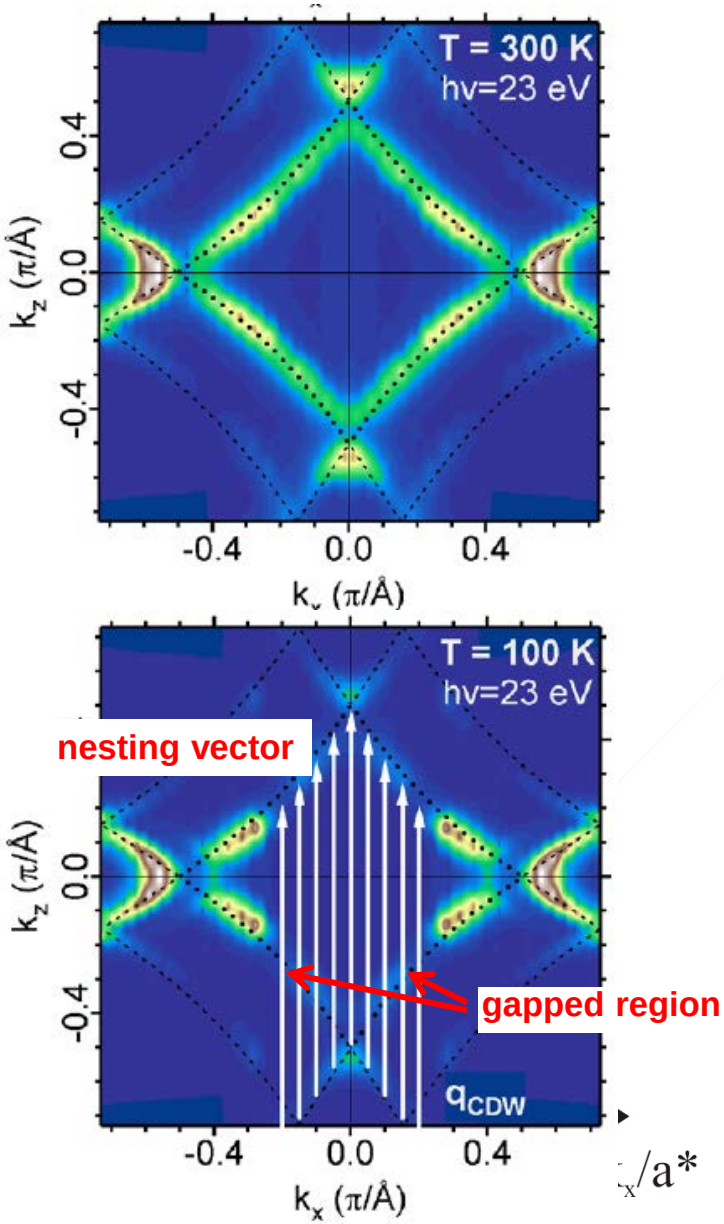
k_x (Å)



Tri-Tellurides – a model CDW system



Fermi surface of $TbTe_3$



Tight-binding model: Te 5p orbitals coupled by $t_{||}$ und $t_{\perp}$

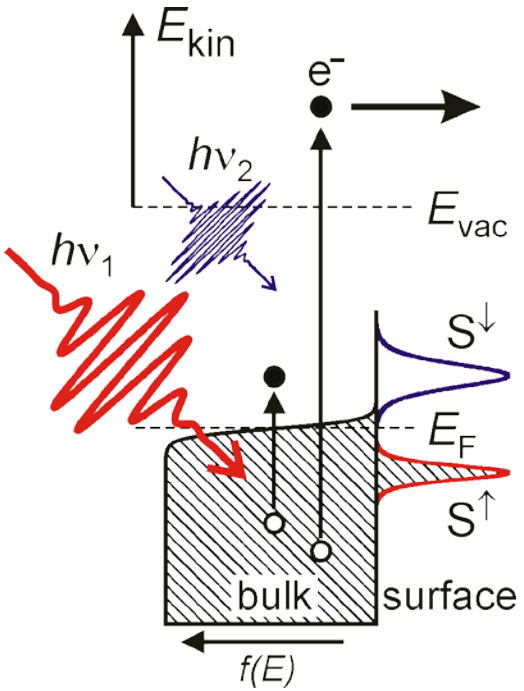
Diamond shaped Fermi surface

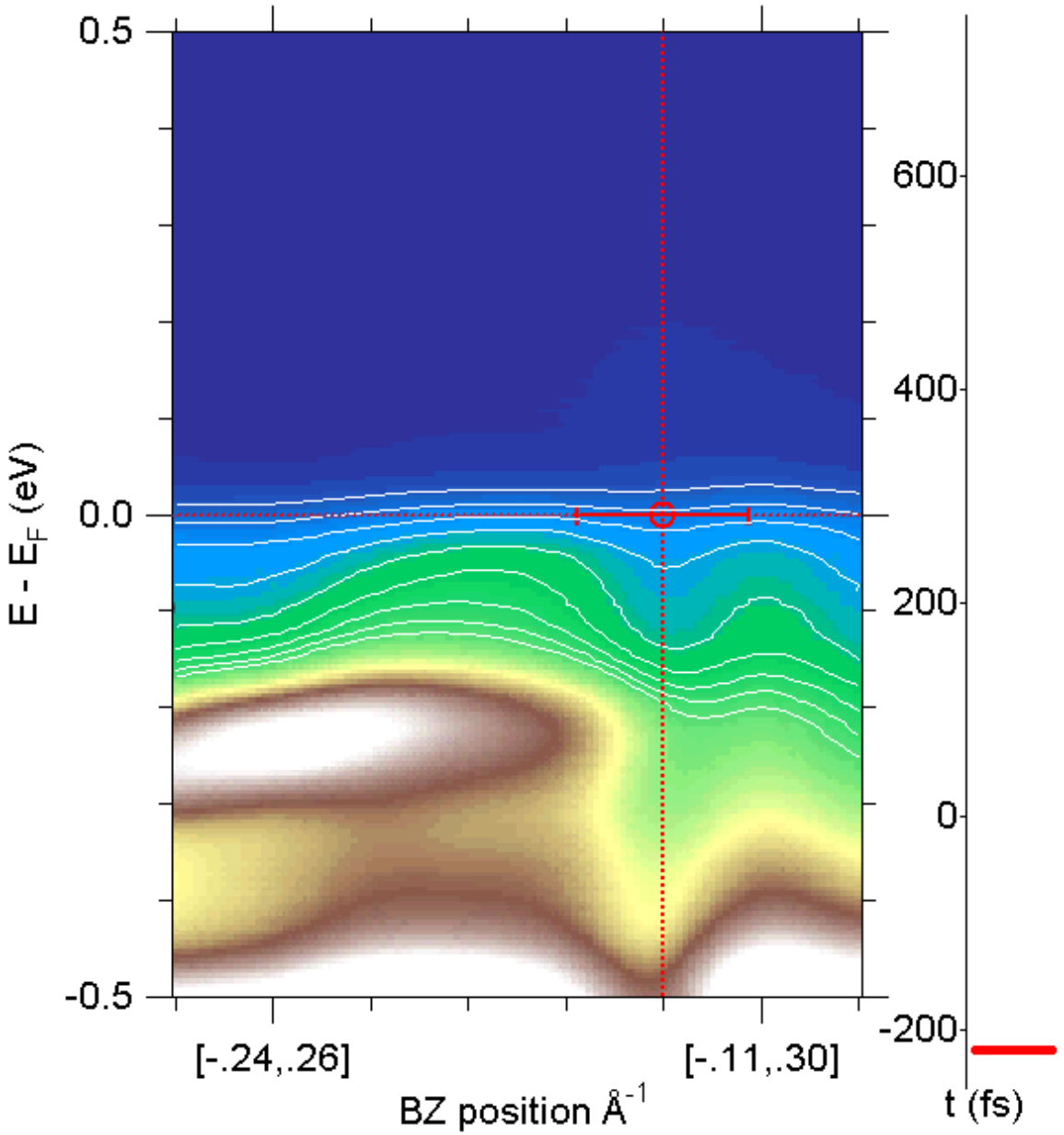
Curvature of bands $\propto$ ratio $t_{\perp}/t_{||}$

V. Brouet, *et al.*, PRL **93**, 126405 (2004)

Transient electronic structure probed by trARPES

Goal: Probe dynamics of electronic structure directly by time-resolved ARPES

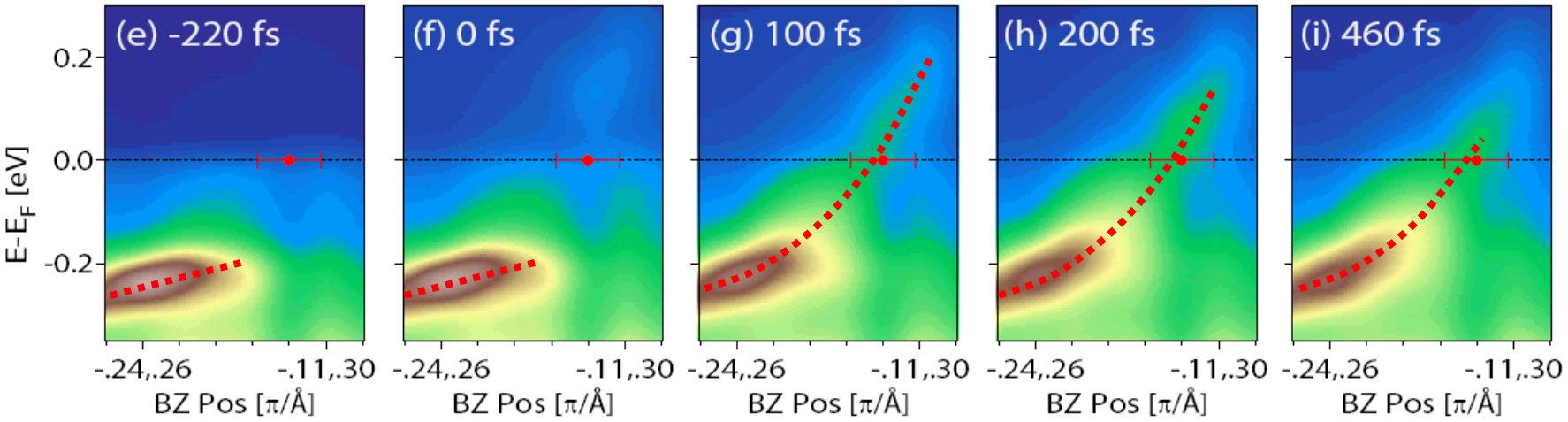




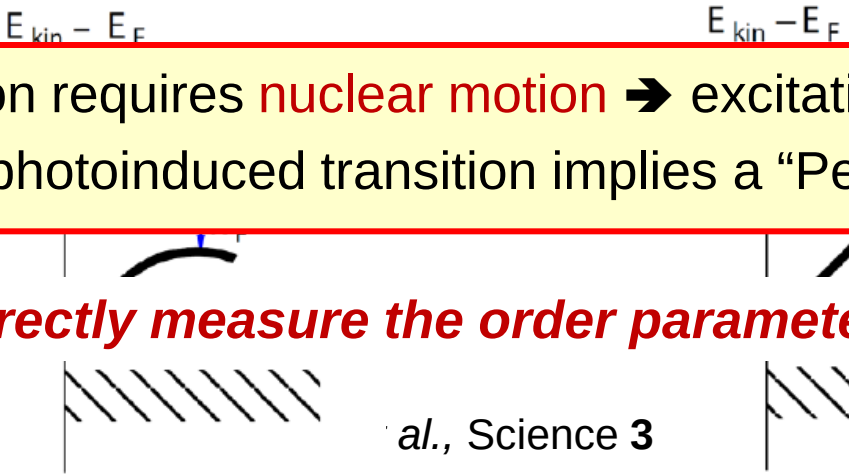
F. Schmitt *et al.*,
Science **321**, 1649 (2008)

Ultrafast electronic melting of CDW state: $TbTe_3$

- Snapshots of electronic structure *E(k)* at different time delays:



- Delayed collaps of CDW gap (>100 fs) after photodoping

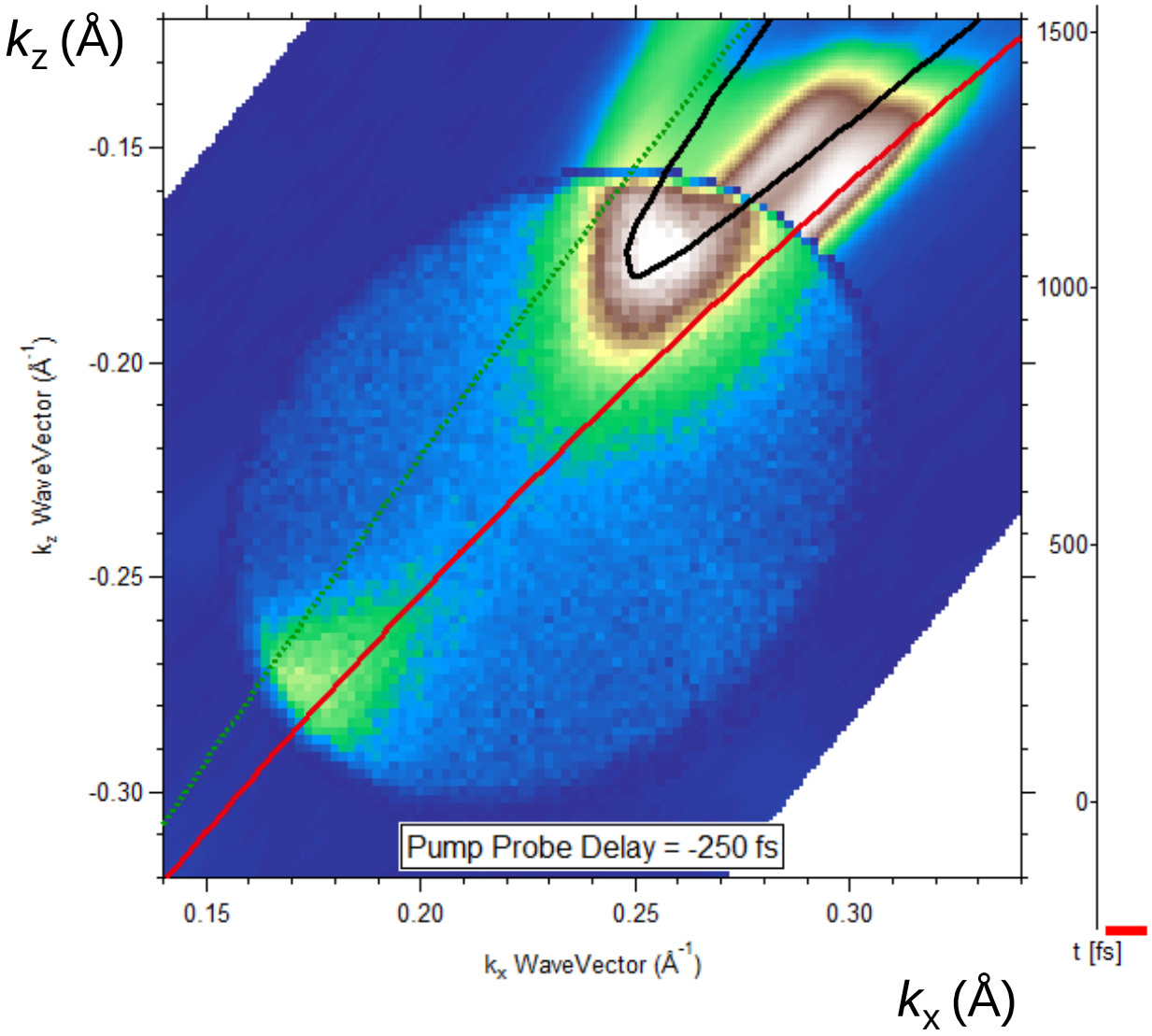


- CDW transition requires nuclear motion ➔ excitation of amplitude mode
- Dynamics of photoinduced transition implies a “Peierls type” scenario

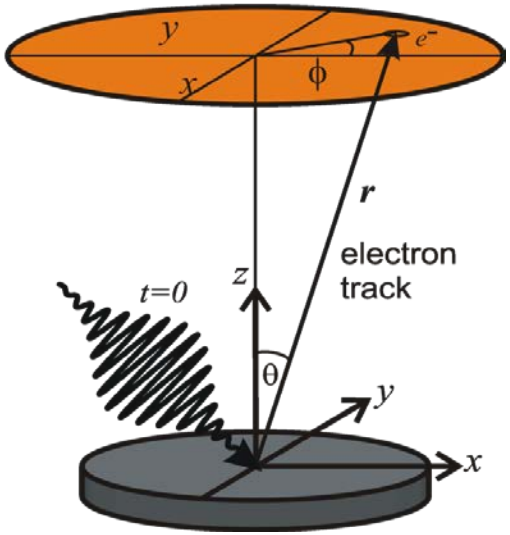
Can we directly measure the order parameter (gap size) ?

al., Science **3**

Time-resolved Fermi surface: $DyTe_3$



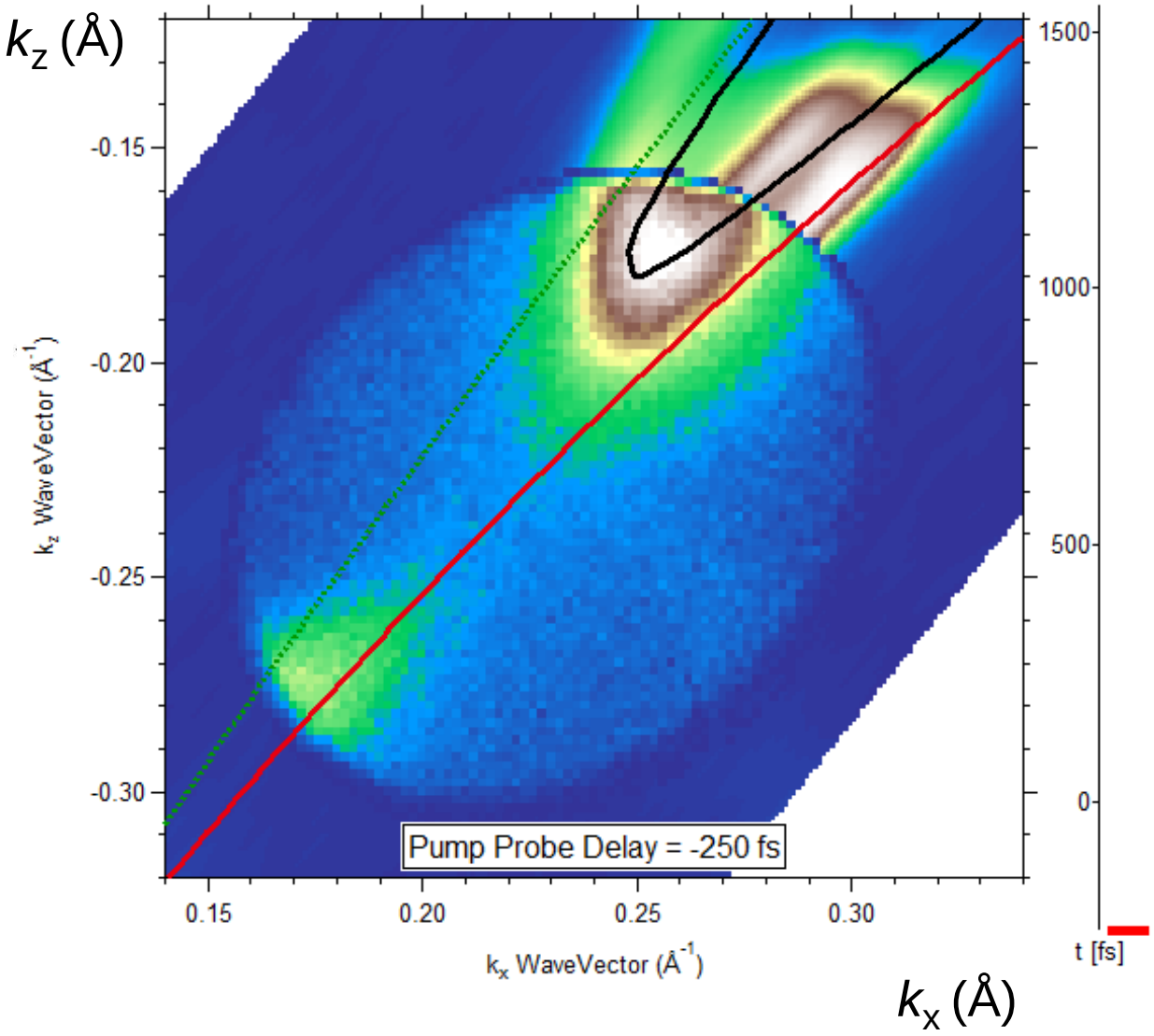
- Gapped area and metallic pocket well resolved with pTOF
- Excellent agreement with 7eV ARPES data and tight-binding model



Appl. Phys A **91**, 211 (2008)

Simultaneous mapping of k_x, k_y, E_{kin} versus time delay Δt

Time-resolved Fermi surface: $DyTe_3$



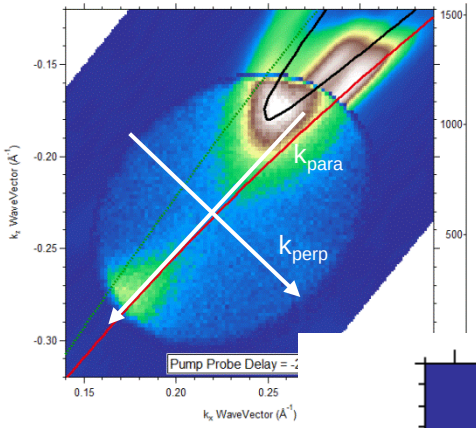
- Gapped area and metallic pocket well resolved with pTOF
- Excellent agreement with 7eV ARPES data and tight-binding model

Dynamics:

- Collapse of the large gap within ~150 fs
- Recovery of metallic Fermi surface (FS)
- Heavy oscillations of intensity near FS

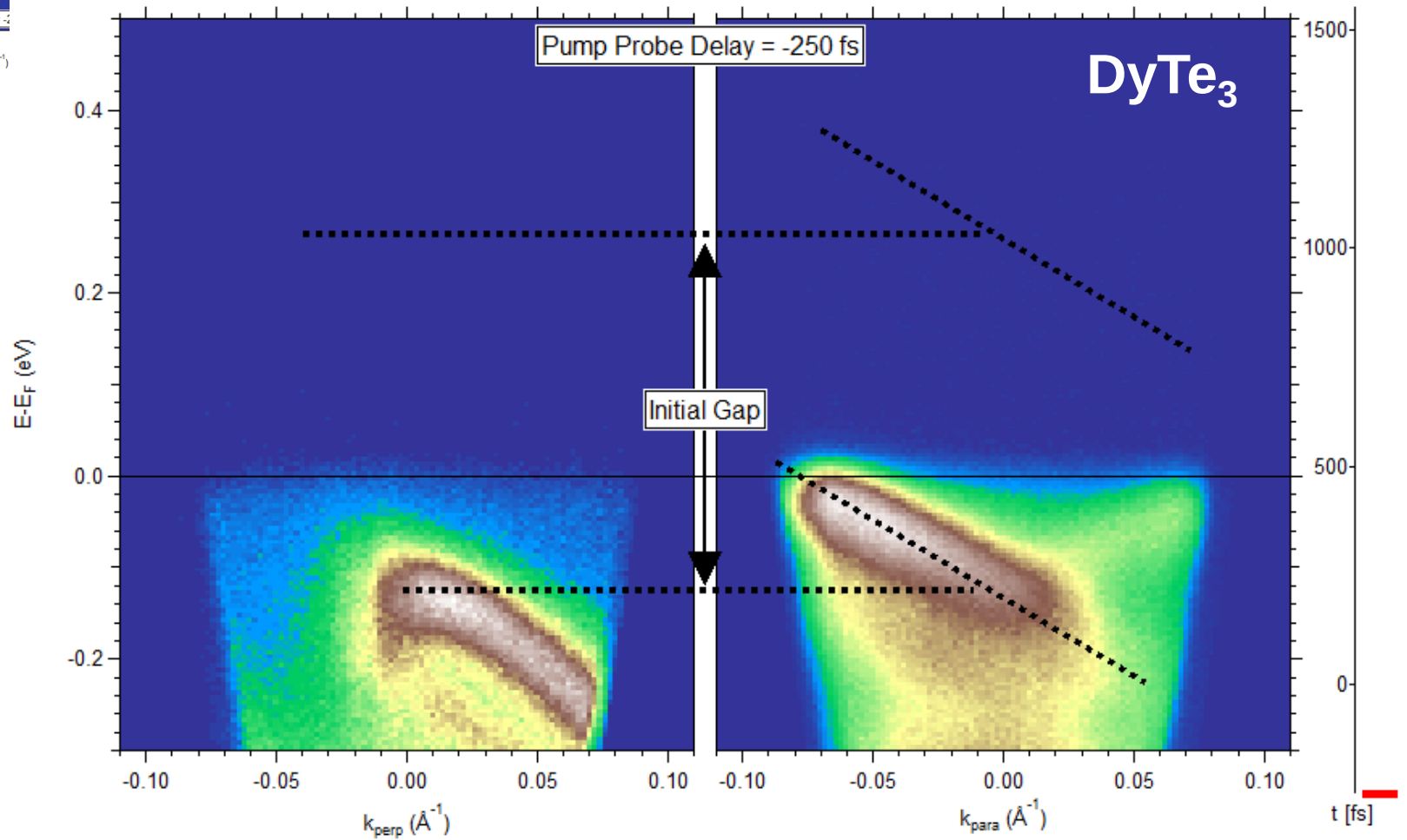
Simultaneous mapping of k_x, k_y, E_{kin} versus time delay Δt

Dynamics along the Fermi surface

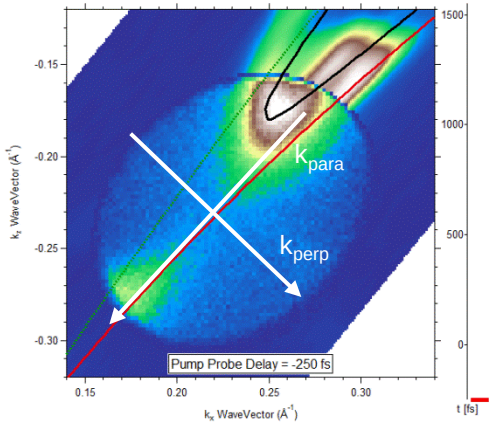


- Transient electronic bandstructure near the gap:
  Dynamics of occupied and unoccupied bands

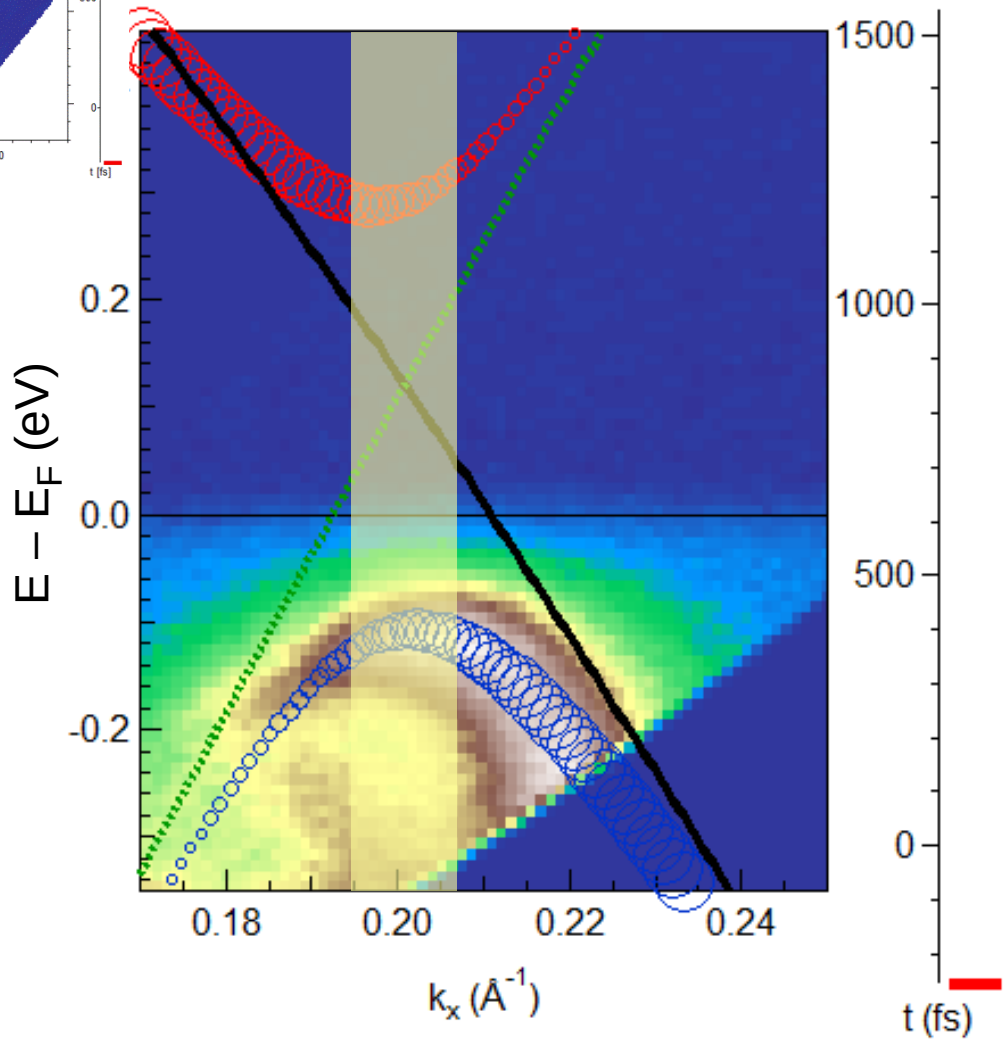
$k_{perpendicular}$ $k_{parallel}$

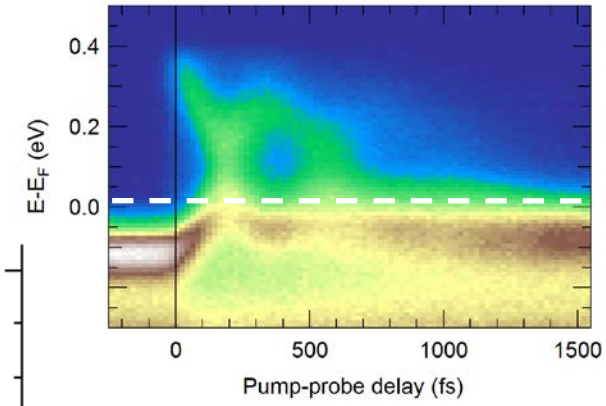


Dynamics of the gapped region: $DyTe_3$



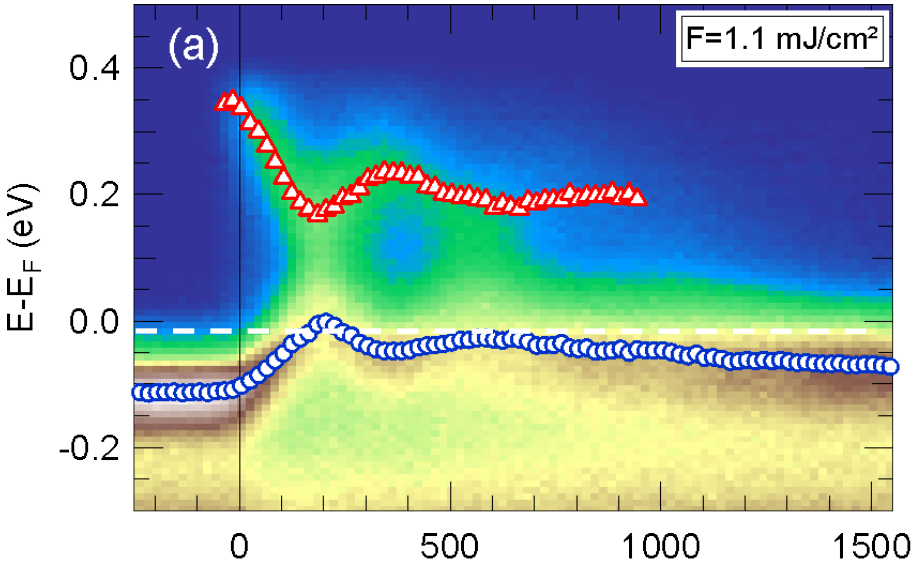
k_x direction



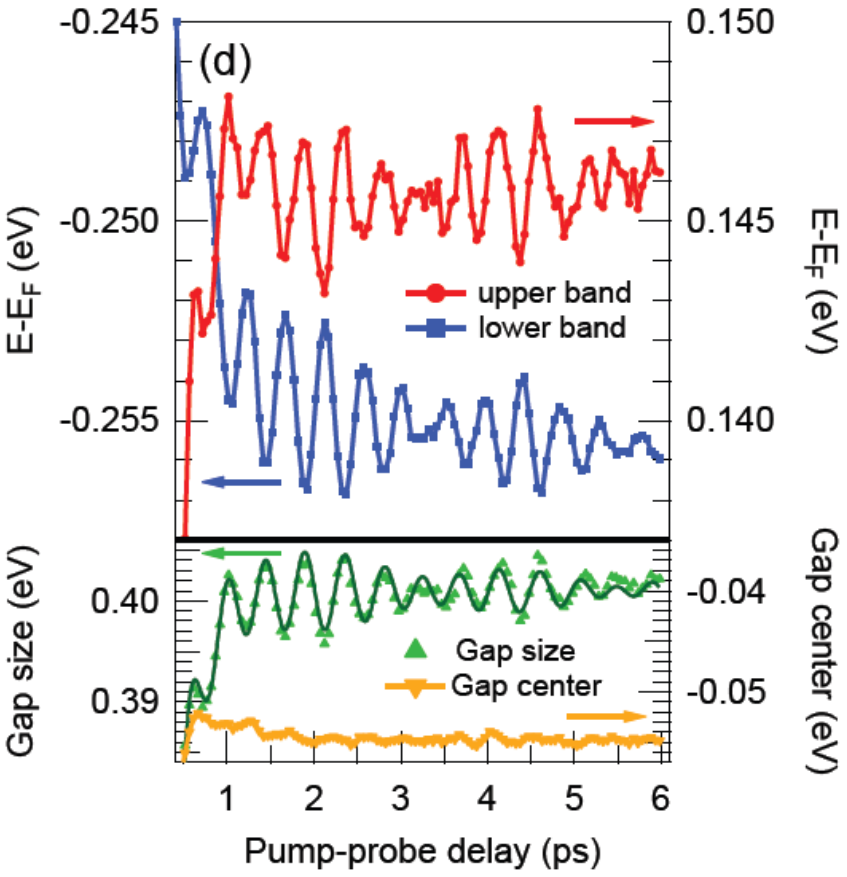


- Population of the unoccupied upper CDW band
- Collaps of CDW gap within ~200 fs
- Transient formation of continuous “metallic” band dispersion
- Fitting to tight binding band structure

Dynamics of the CDW band gap



- Transient evolution of the lower and upper CDW band
- Pronounced oscillations of the ions in potential of the excited CDW system: **amplitude mode**

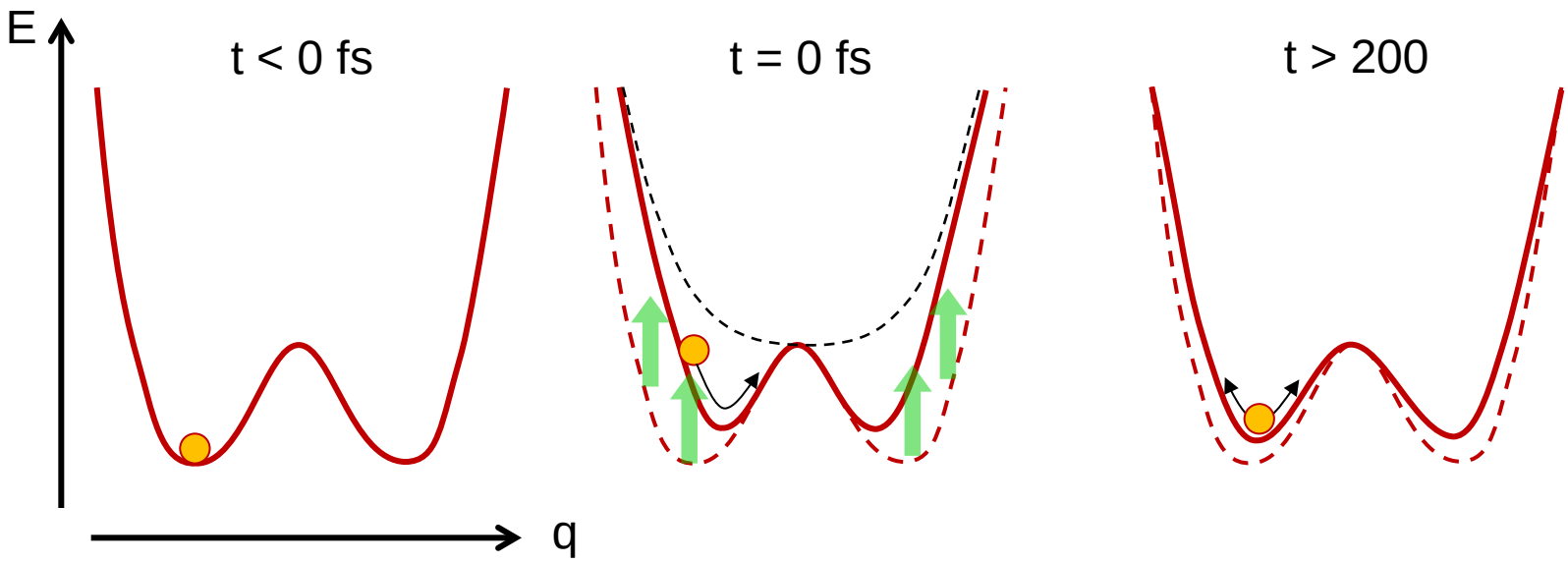


Conclusion:

- **Insulator-to-metal transition** (lower CDW band shifts above E_F)
- At least **two phonon modes** modulate the CDW gap indicating a complex dynamics in the excited state.)

Discussion: CDW amplitude mode

- Schematic sketch of the CDW potential energy surface



CDW ground state

electronic excitation

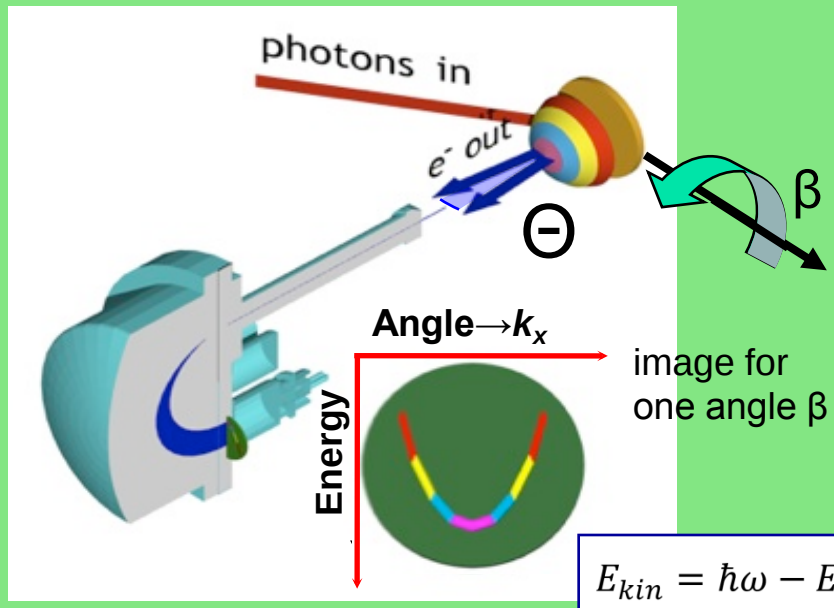
periodic oscillation of amplitude mode & CDW gap size

- CDW order parameter remains finite in photoexcited state
- Multiple phonon modes modulate the CDW gap

L. Rettig *et al.*, Faraday Discuss. **171**, 299 (2014) & Nature Commun. **7**, 10459 (2016)

Probing the full Brillouin zone: XUV-based trARPES

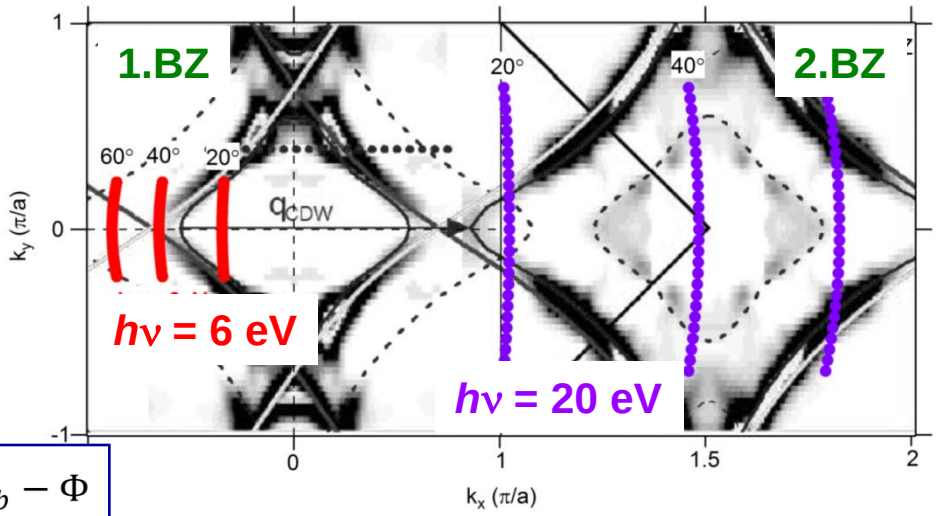
Goal: Probing transient electronic structure of solids throughout k-space



$$E_{kin} = \hbar\omega - E_b - \Phi$$

$$\hbar k = \sqrt{2m_e E_{kin}}$$

k-space access to full Brillouin zone



***k*-space access examplified for $CeTe_3$ at hν = 6 eV and hν = 20 eV.**

Desired parameters of trARPES photon source:

- Sufficient photon energy to **access full Brillouin zone**, i.e. hν >10 eV
- High repetition rate providing **good counting statistics**, i.e. >100 kHz
- **Time resolution**: from few fs to several 10 fs pulse duration
- Flexibility in time-bandwidth product: **Adapted** energy resolution

Development of 500 kHz OPCPA System

Yb fiber oscillator
>100 mW; 25 MHz
1030 nm
10 nm FWHM

STRETCHER
CVBG
12.5 ps/nm

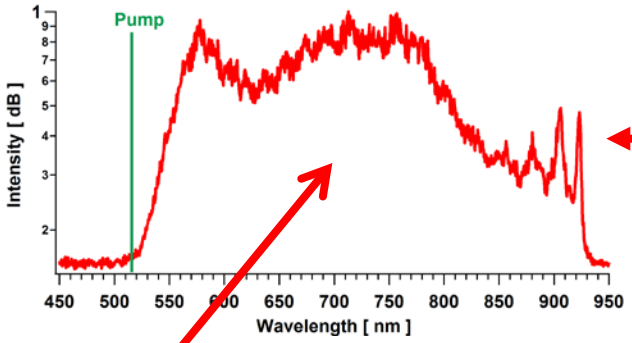
FIBER AMPLIFIER
9.2 W; 500 kHz
1030 nm
8 nm FWHM

BS

Pump

innoSLAB AMPLIFIER
200 W; 500 kHz
1030 nm
1 nm FWHM

Signal



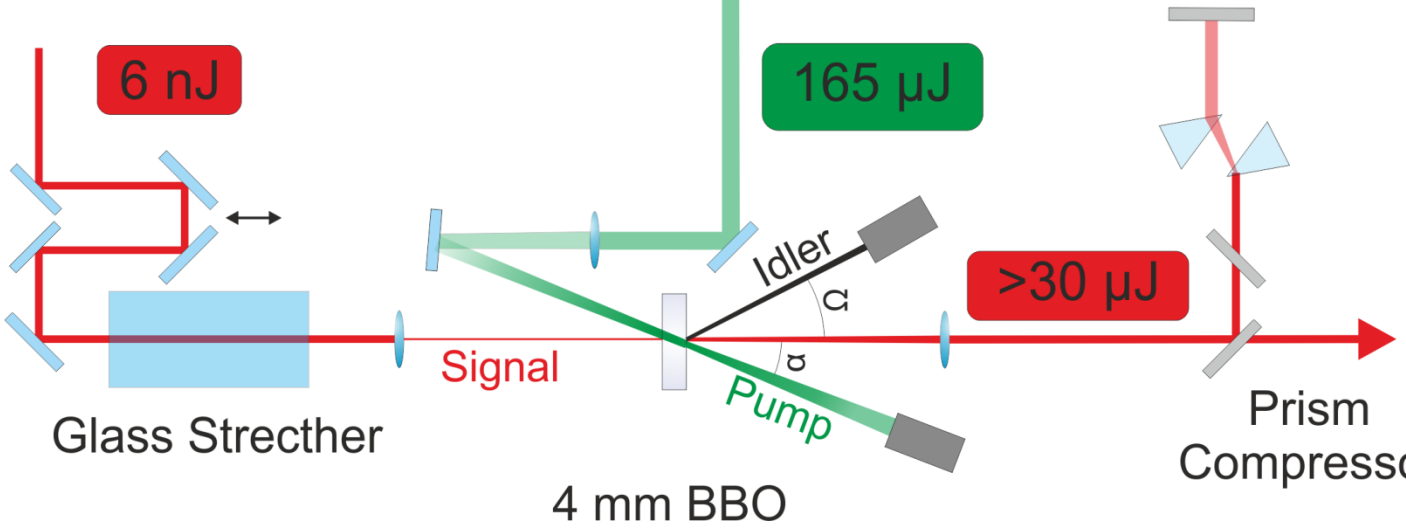
COMPRESSOR 1
CVBG &
Transmission gratings
360 fs

SHG: PUMP
3 mm BBO
η=55%; 82.5 W
515 nm

COMPRESSOR 2
Transmission gratings
T=75%; 160 W
1.25 ps

White-light generation in YAG (4 mm)

⇨ Passive optically synchronized laser system

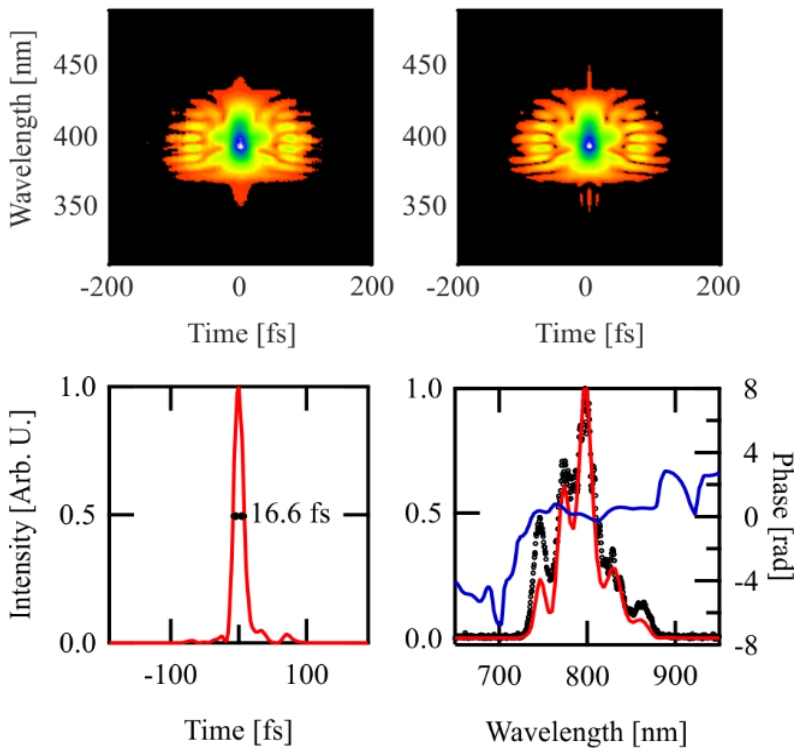


Puppin *et al.*, Opt. Expr. 23, 1491 (2015)

Walk-off compensated configuration

Development of 500 kHz OPCPA System

Compresssed OPCPA output:



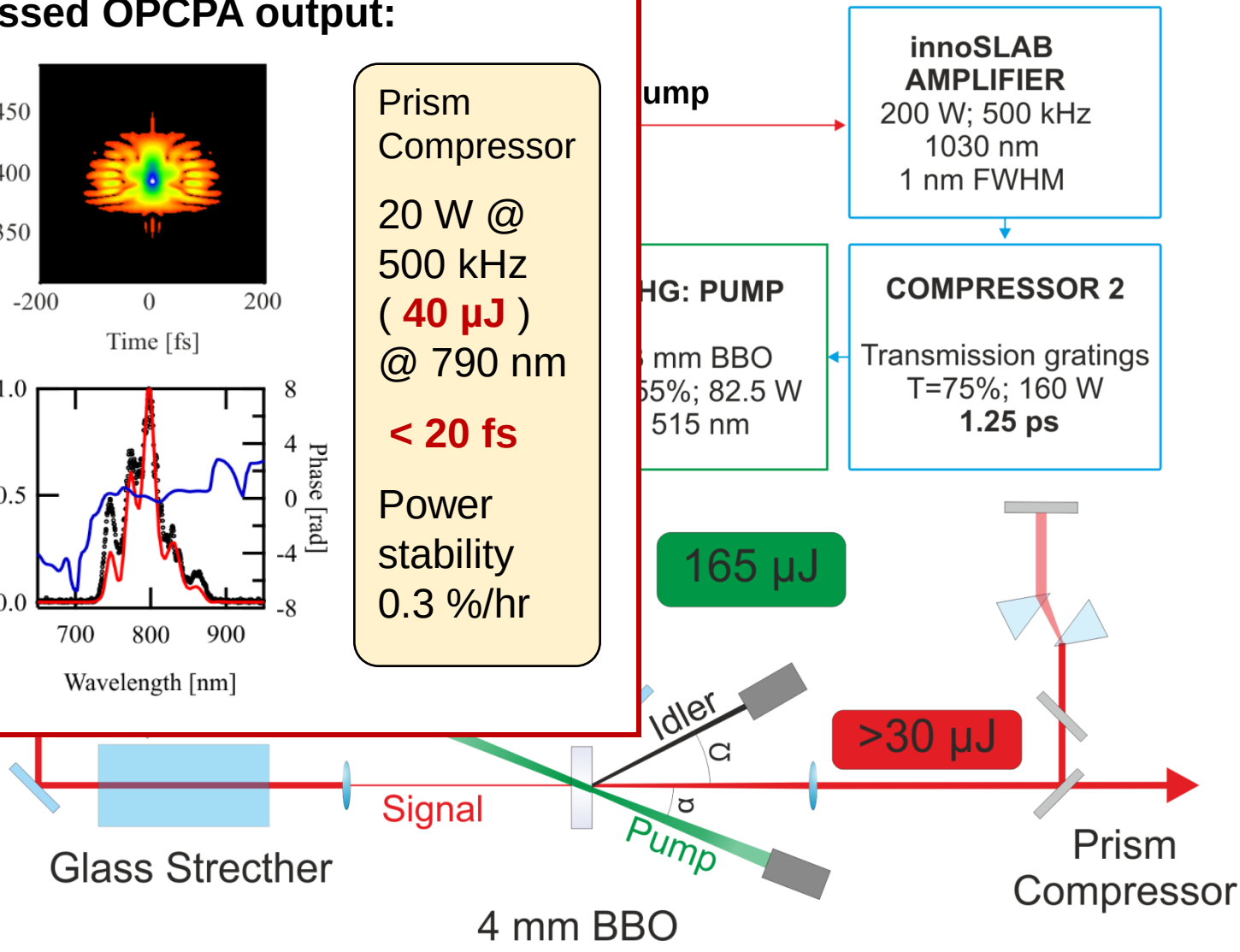
Prism Compressor

20 W @ 500 kHz (**40 µJ**) @ 790 nm

< 20 fs

Power stability 0.3 %/hr

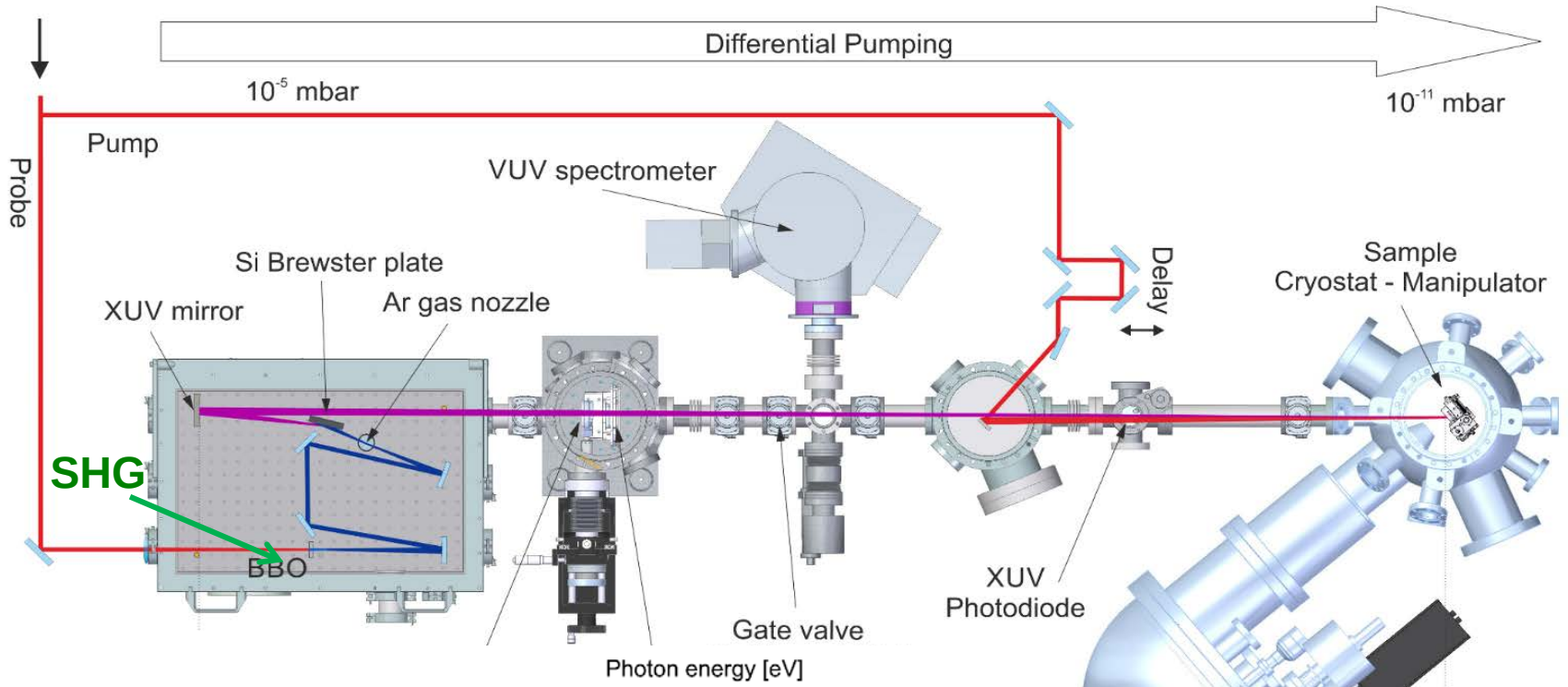
synchronized laser system



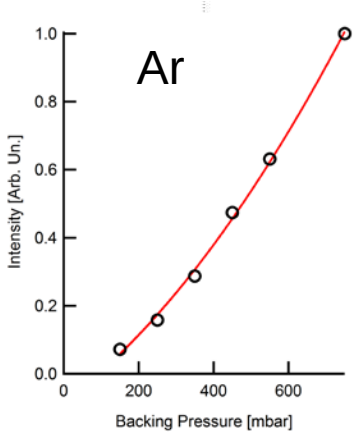
Puppin *et al.*, Opt. Expr. 23, 1491 (2015)

Walk-off compensated configuration

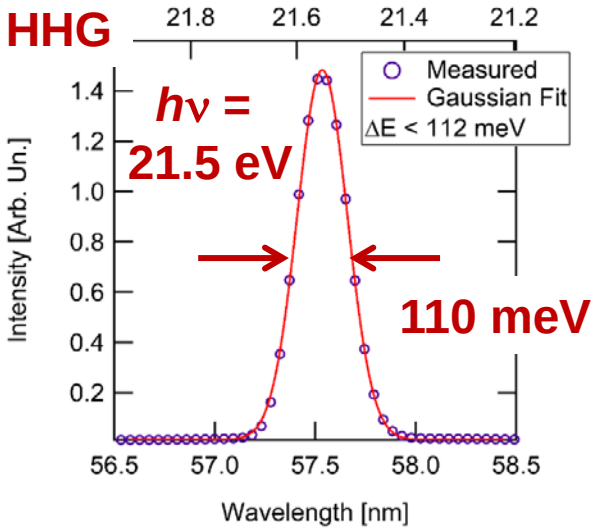
XUV-based time-resolved ARPES setup



pressure scaling:



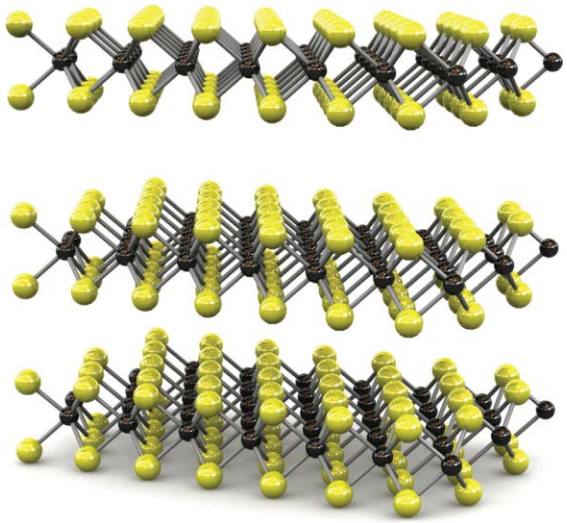
HHG



400 nm-driven HHG in Ar:
7th harmonic (at 21.5 eV)
>10^11 photons/s at sample
within ~100 meV bandwidth

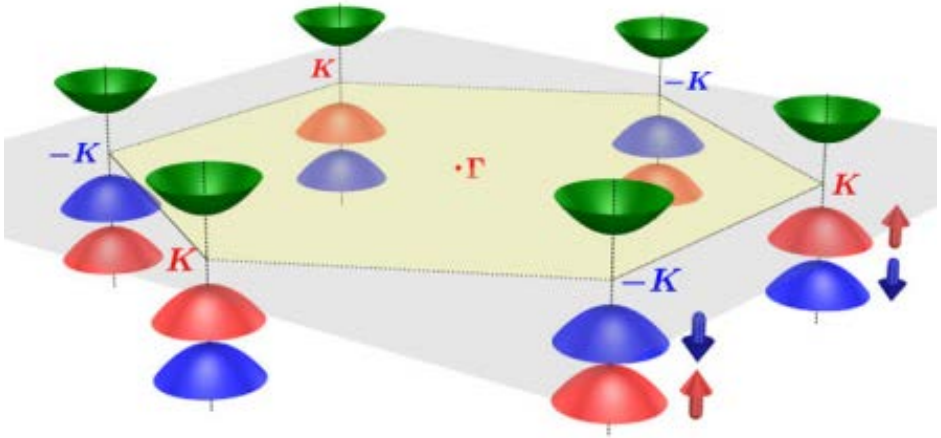
Semiconducting transition metal dichalcogenides

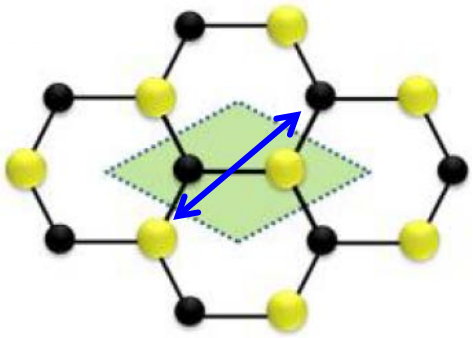
General characteristics: **layered crystals, about 40 different TMDCs**



Examples:

- MoS_2
- WSe_2





No intra-layer inversion symmetry

Pronounced excitonic effects:

- up to several 100 meV binding energy for freestanding monolayers

Pronounced spin-orbit splitting:

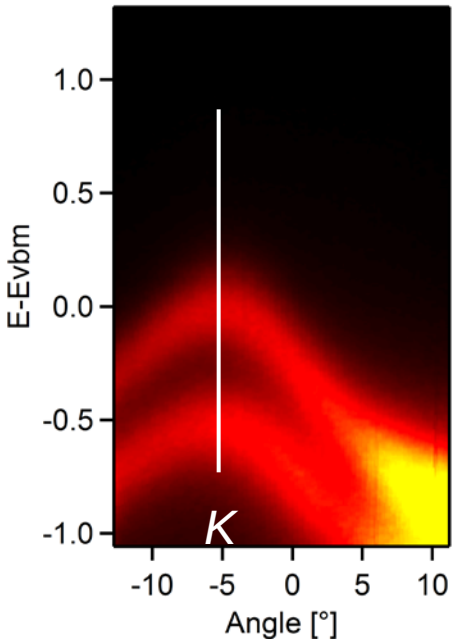
- up to 500 meV spin splitting in valence band

Peculiar electronic structure:

- spin-, valley- and layer degrees of freedom
- pronounced *k*-dependence

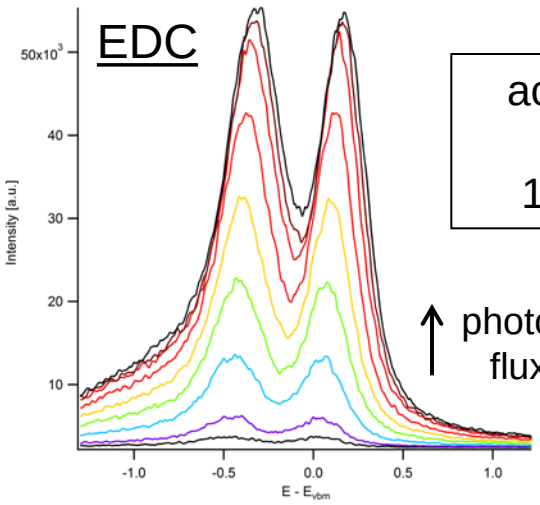
500 kHz HHG-based ARPES

Occupied bands, K valley WSe_2



acqu
tir
60

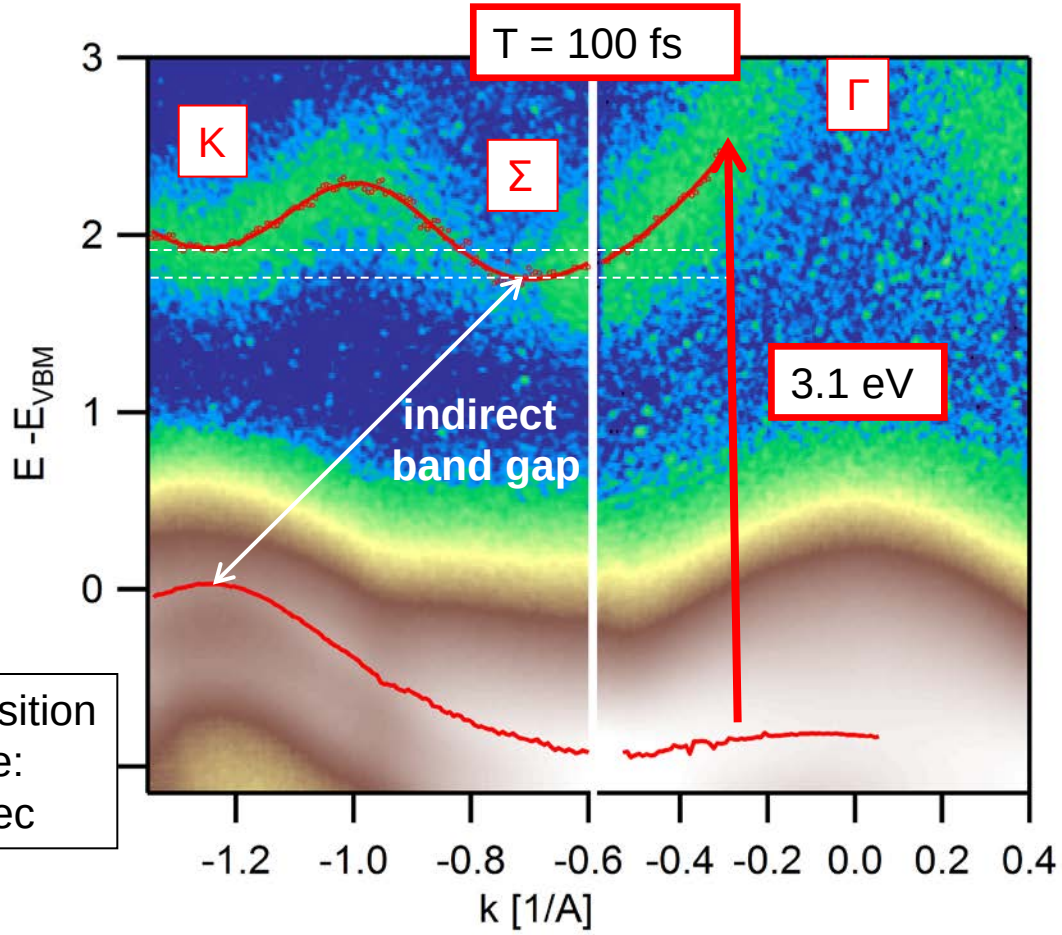
EDC



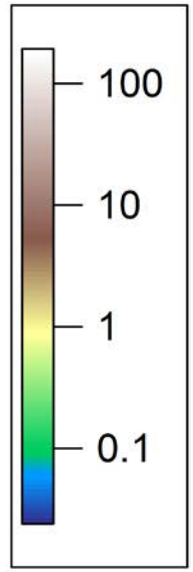
acquisition time:
10 sec

photon flux

Excited state mapping in WSe_2
(**Δt = 50 fs**, 3 eV pump, "full k-space")



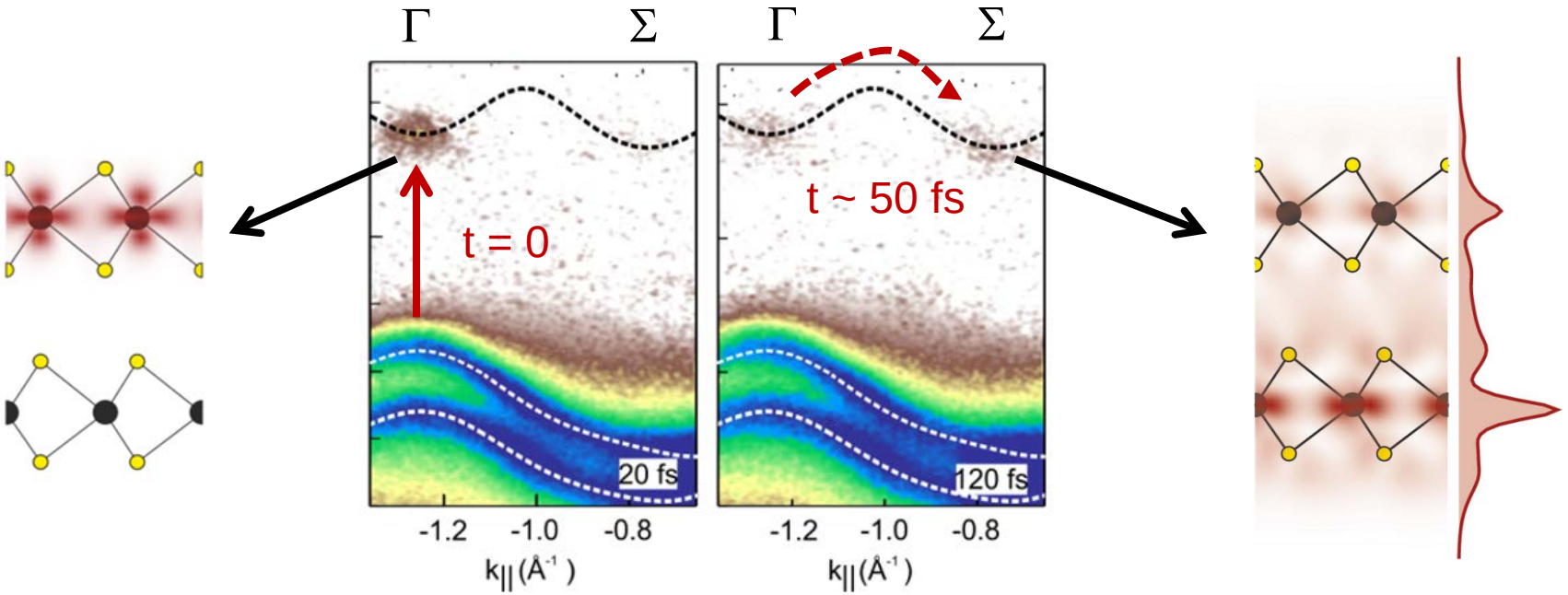
log scale



Direct mapping of conduction band (excited states)

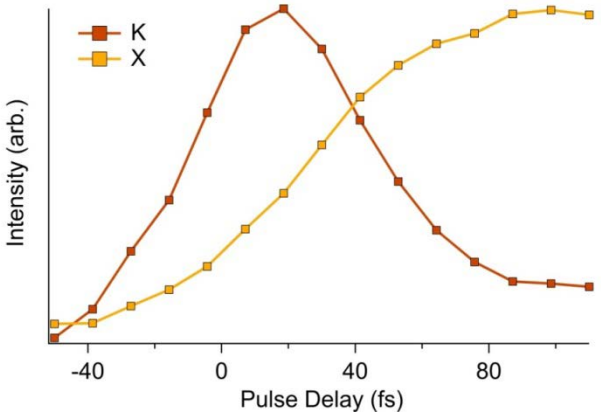
Excited state dynamics in WSe_2

Projection of spin-, valley- and layer-polarization on excited states



→ Intervalley scattering transfers population from 2D to 3D states.

→ These states govern interlayer coupling, transport, …



Ultrafast surface chemistry

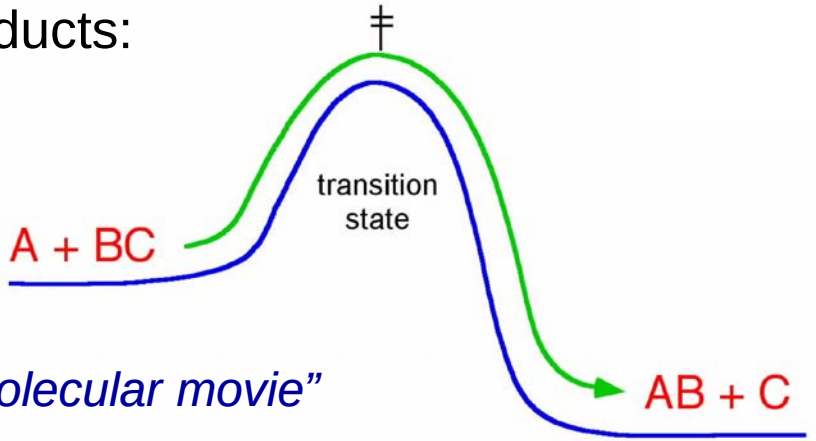
Probing chemical bond formation at surfaces by femtosecod x-ray spectroscopy

Dell'Angela *et al.,* Science **339**, 1302 (2013)

H. Öström *et al*., Science **347**, 978 (2015)

Dynamics of chemical reactions

Temporal evolution from reactants to products:



- Dynamics of the transition state
- Key concept: Born-Oppenheimer potential energy surface
- Molecular dynamics simulations: *"molecular movie"*

However, the forces originate from the electronic structure !

Open questions:

- Dynamics of the electronic structure associated with the nuclear motion
- Non-adiabatic coupling between electronic states (e.g. at conical intersections)

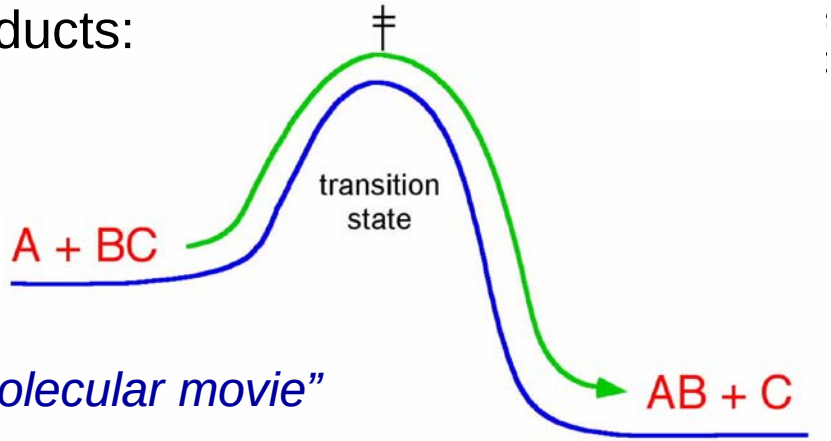
Movie of transient electronic structure

Goal: Microscopic understanding of reaction dynamics

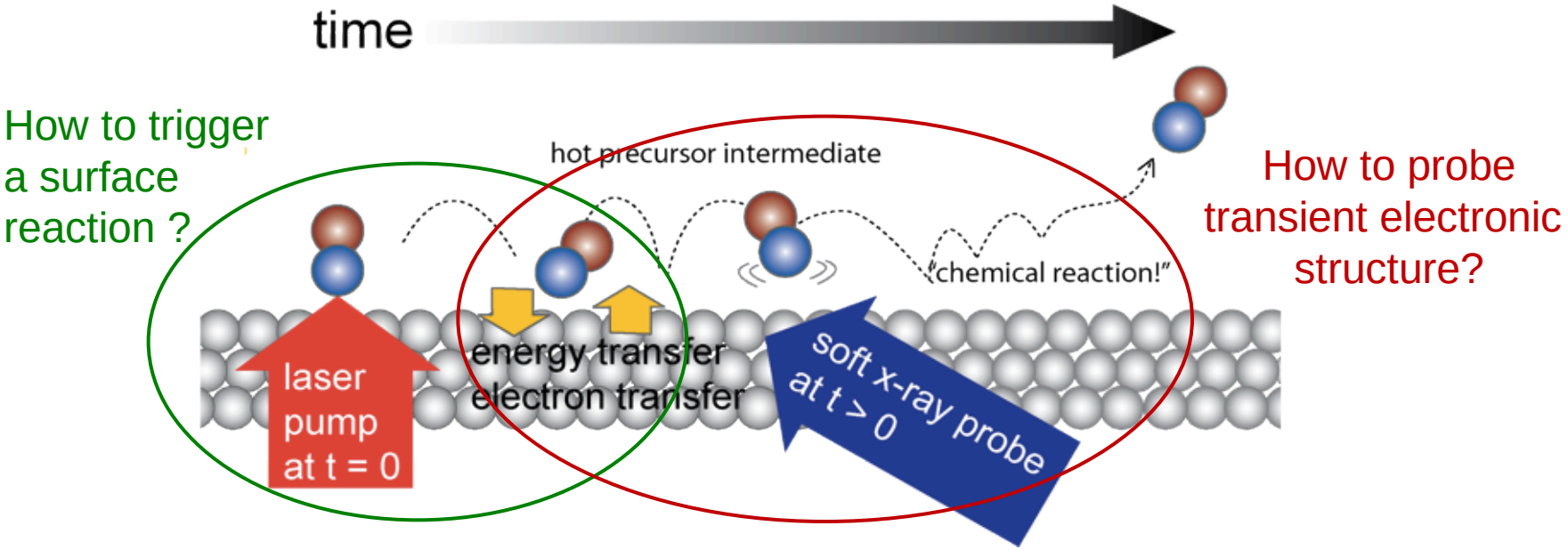
Dynamics of chemical reactions

Temporal evolution from reactants to products:

- Dynamics of the transition state
- Key concept: Born-Oppenheimer potential energy surface
- Molecular dynamics simulations: *"molecular movie"*

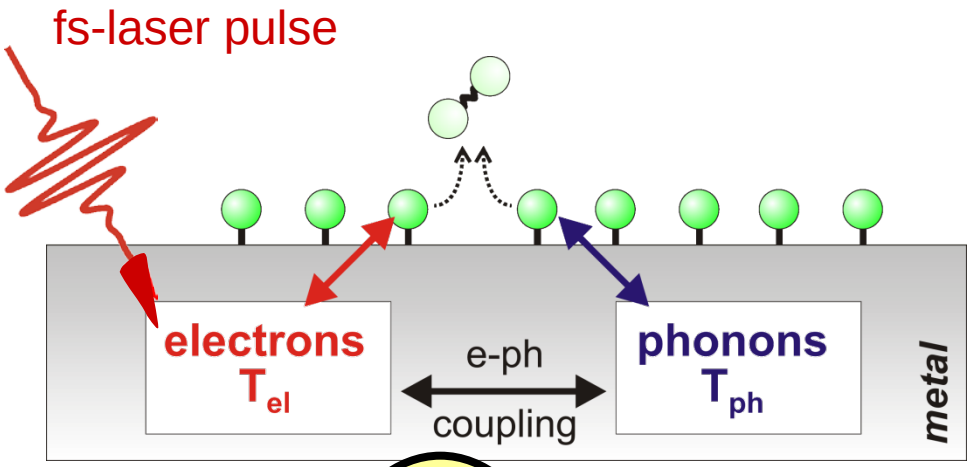


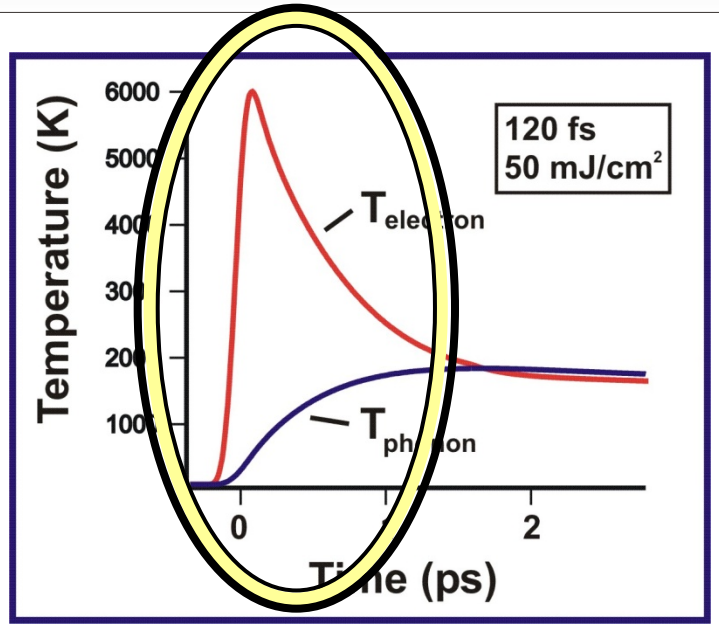
Goal: Evolution of the transient electronic structure, *e.g. during a surface reaction*



Femtochemistry at metal surfaces

Ultrafast energy redistribution after optical excitation of a metal surface





- monolayer is optical thin
- substrate-mediated excitations dominate

transient non-equilibrium with T_{el} >> T_{ph}

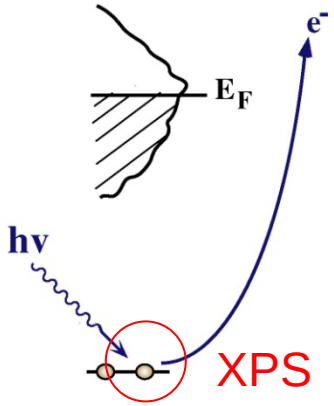
coupling to adsorbate vibrations induces reaction

reaction driven by electrons (fast) or phonons (slow)

Review: Ch. Frischkorn & M.Wolf, Chem. Rev. 106, 4207 (2006)

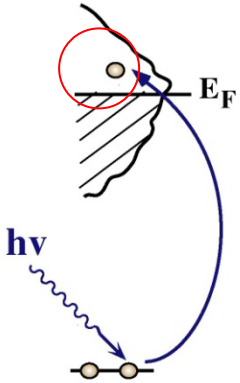
Photon in – photon out methods: X-ray emission

X-ray photoemission (XPS)

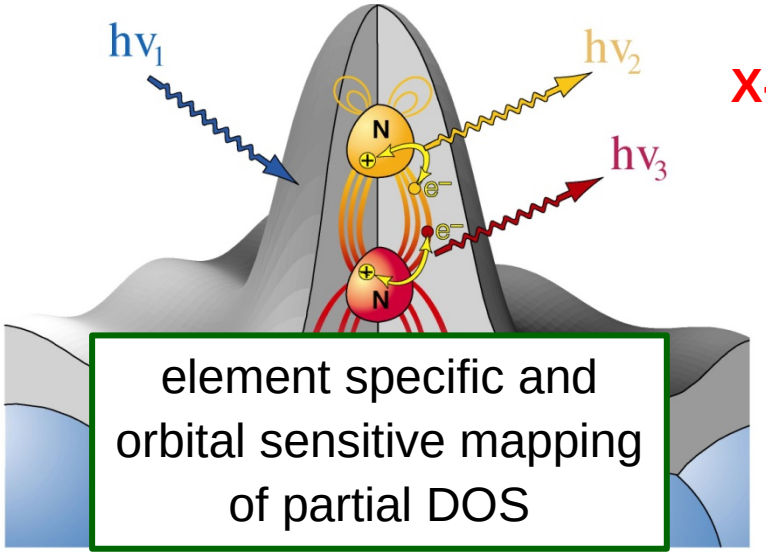


Probe chemical state

X-ray absorption (XAS)

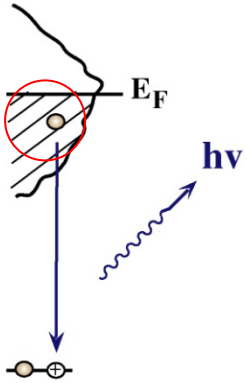


unoccupied valence state



element specific and orbital sensitive mapping of partial DOS

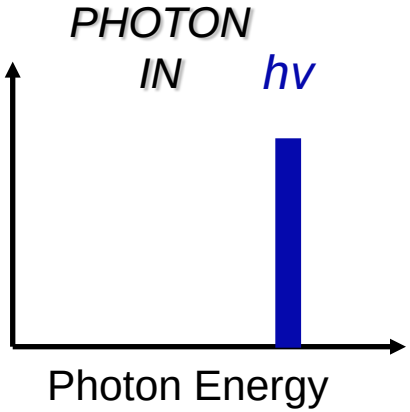
X-ray emission (XES)

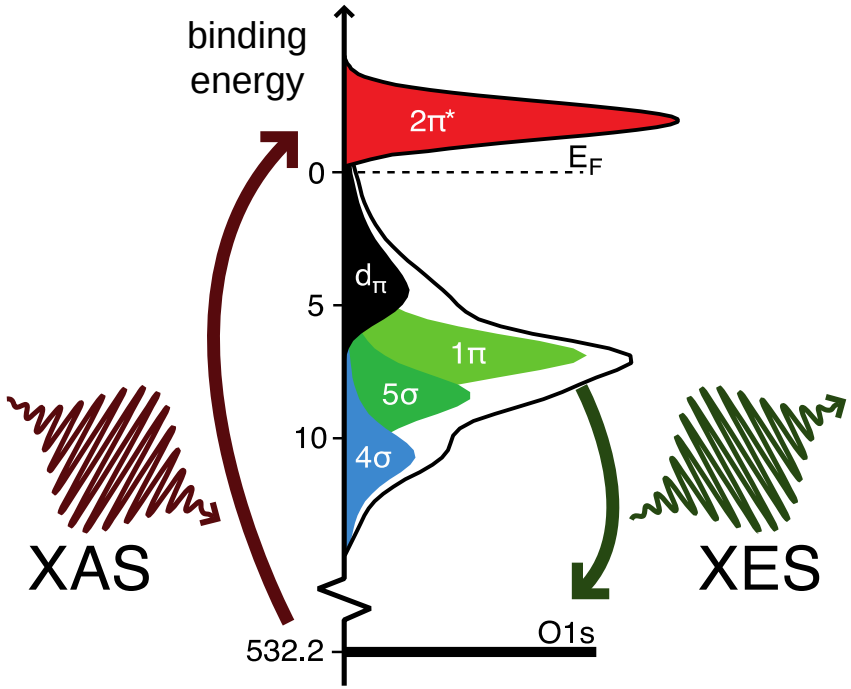


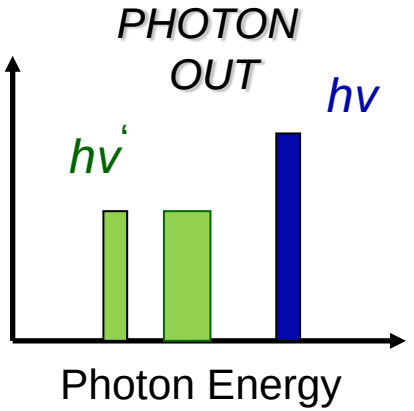
occupied valence state

A. Nilsson, Surf. Sci. Rep. 55, 49 (2004)

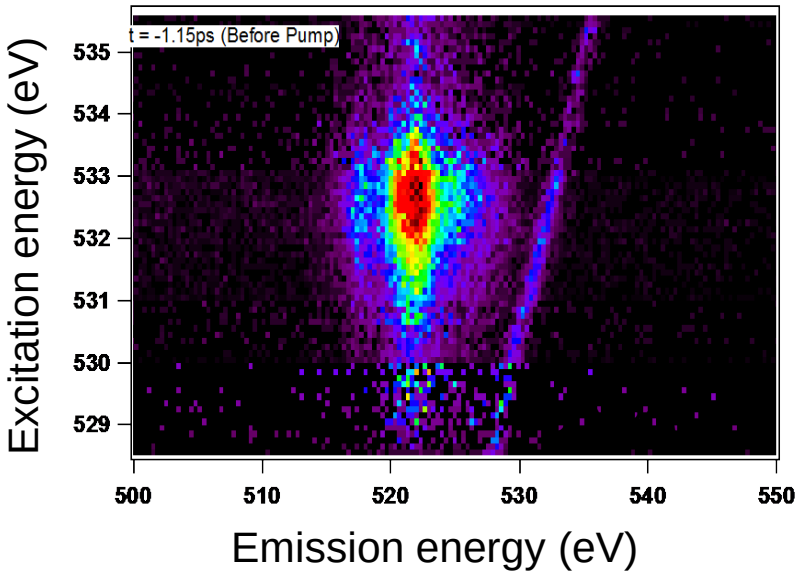
Resonant inelastic X-ray scattering (RIXS)





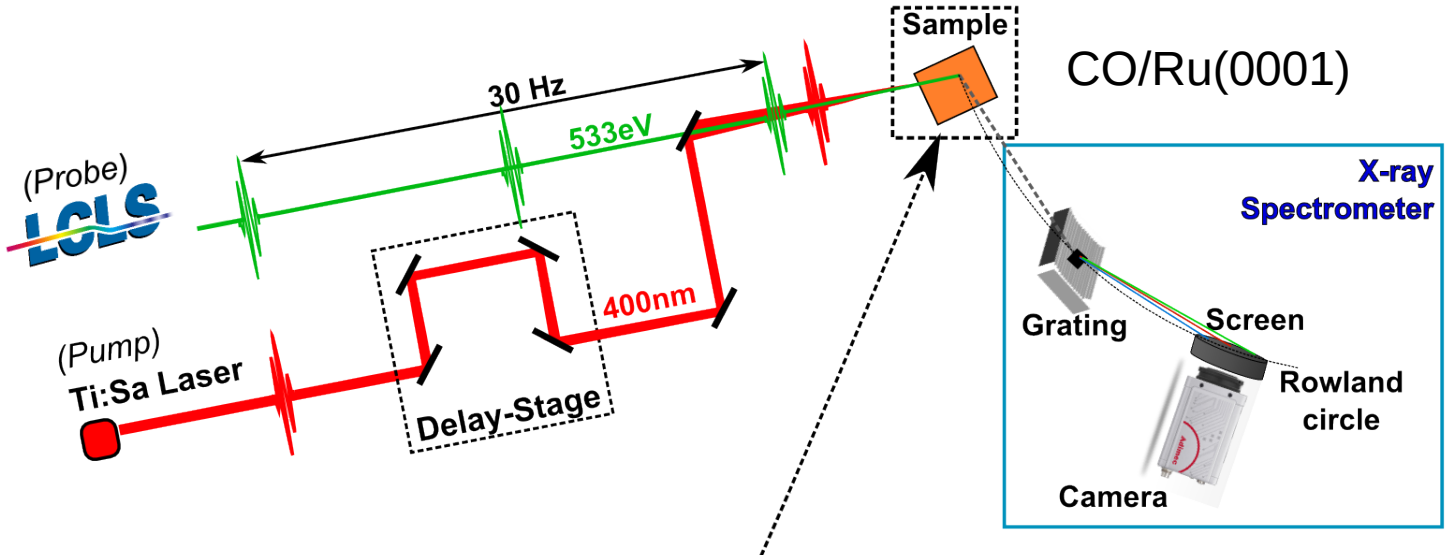


scan excitation energy

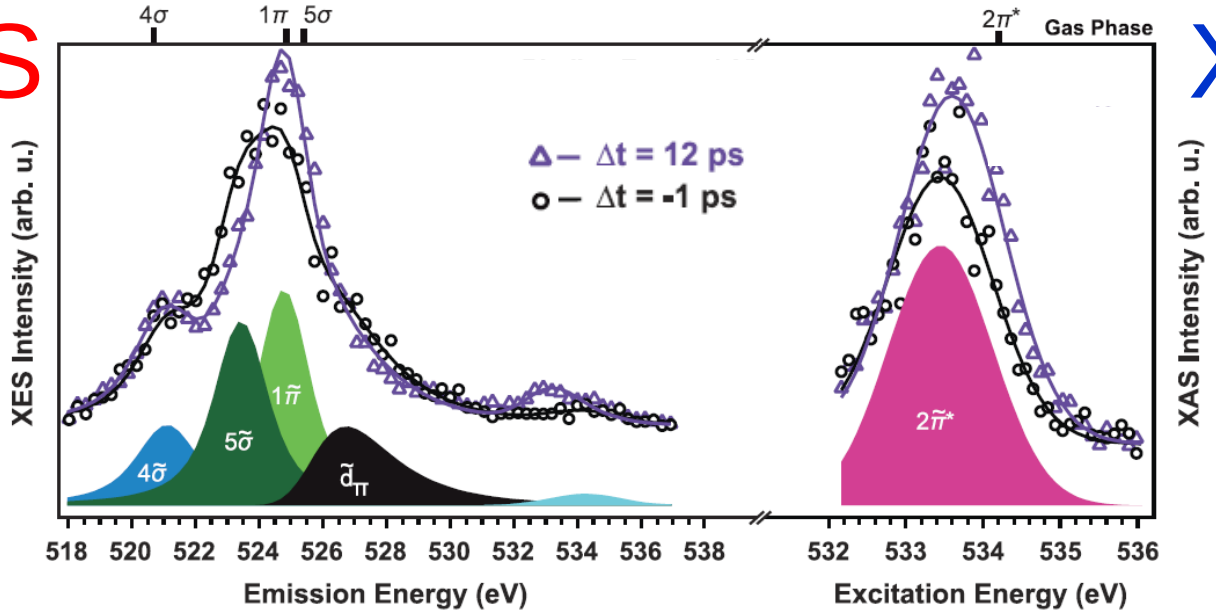


probe x-ray emission energy

Time-resolved RIXS of laser-excited CO/Ru(0001)



XES



XAS

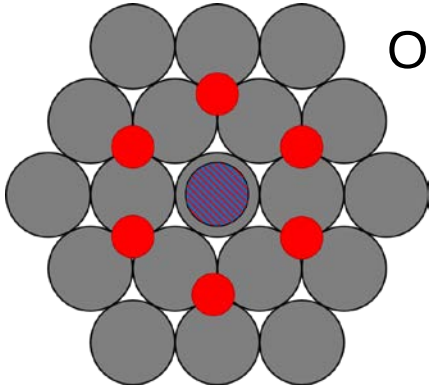
Dell'Angela *et al.* Science **339**, 1302 (2013)

fs-laser-induced CO oxidation probed by trXAS

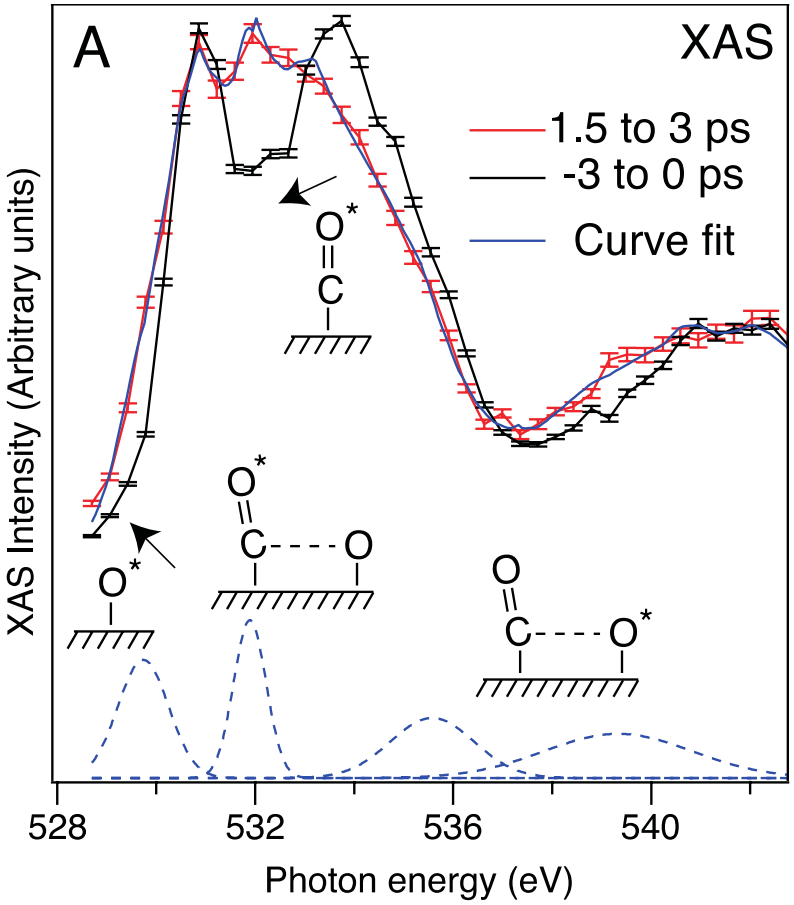
X-ray laser

Optical laser

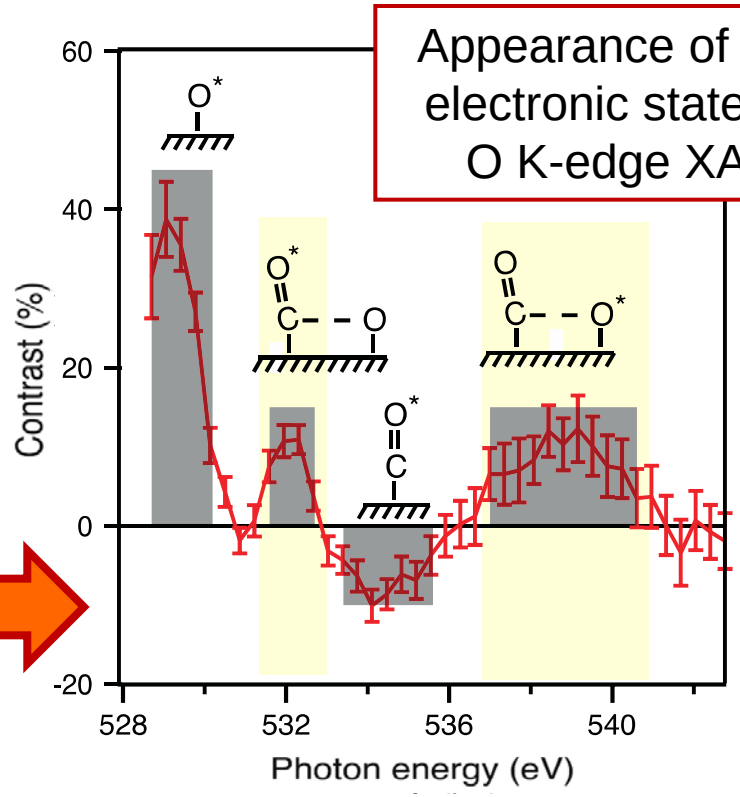
Δt



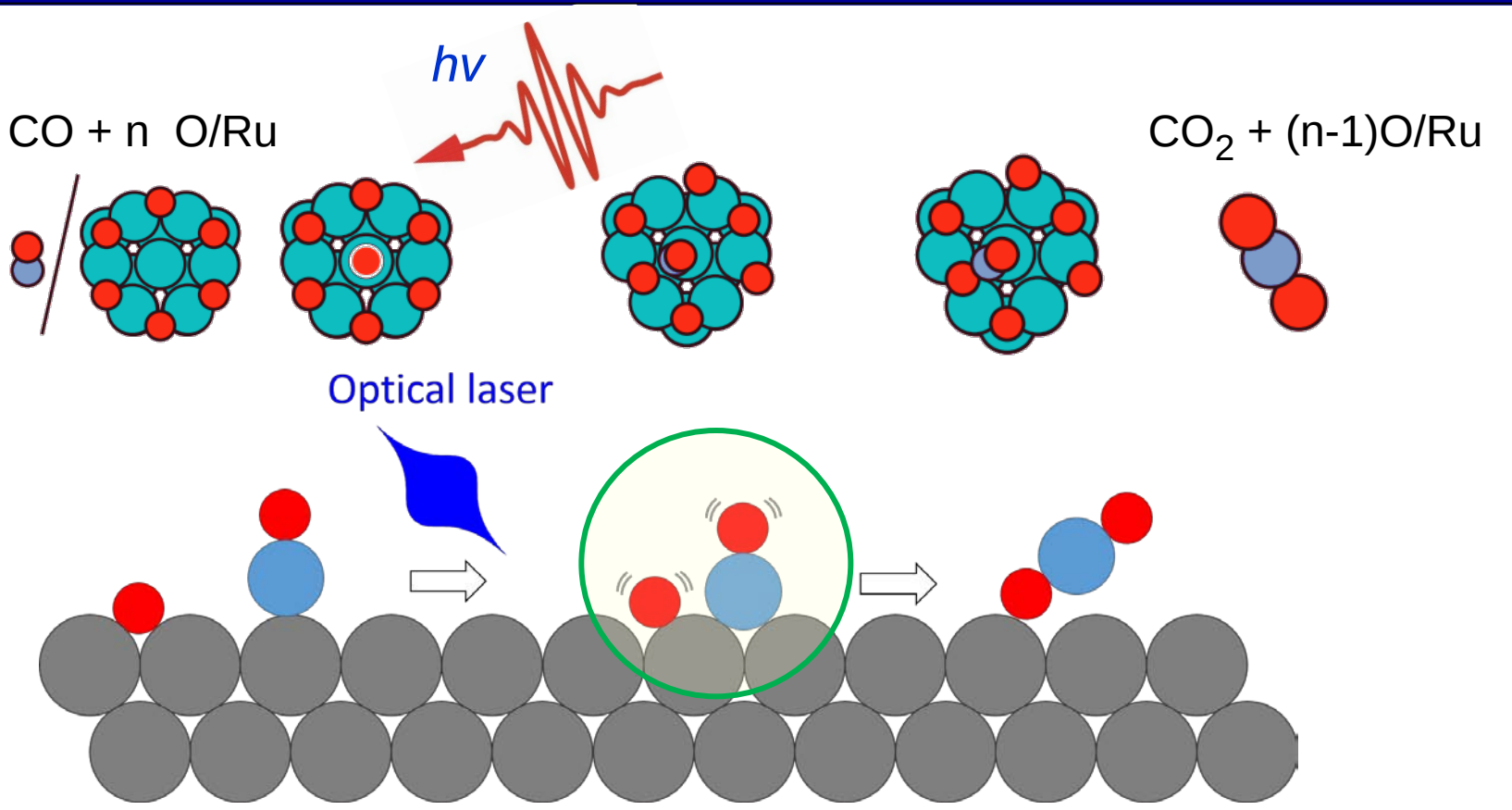
O + CO / Ru(001)



Appearance of new electronic states in O K-edge XAS



Summary: Dynamics of CO oxidation



- Both O and CO are excited and „collide“ in reactive adlayer during CO_2 formation: Formation of transient OC–O species
- Distribution of OC–O bond lengths close to transition state
- Transition state region is more complex than previously believed

H. Öström et al., Science 347, 978 (2015)

Summary

- Various elementary processes in physics, chemistry, biology occur on femtosecond time scales.
- Femtosecond laser pulses exhibit unique properties for metrology of light, non-linear optics, ultrafast spectroscopy & more.
- Examples:
  - Time-domain THz spectroscopy of photoexcited carriers.
  - THz pumping of low frequency modes (magnons, phonons)
    ⇨ an unconventional way to couple energy into the system
  - Dynamics of electronic band structure in solids probed by trARPES
- There exists a large toolbox to induce and probe ultrafast dynamics in solids and at interfaces (THz to x-rays, electrons,…)
- These tool have specific strengths, but also limits…